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A TEXT-BOOK  
OF  
VOLUMETRIC ANALYSIS

WITH SPECIAL REFERENCE TO  
THE VOLUMETRIC PROCESSES OF THE  
PHARMACOPŒIA OF THE UNITED STATES.

DESIGNED FOR THE USE OF PHARMACISTS  
AND PHARMACEUTICAL STUDENTS.

BY

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the Brooklyn College of Pharmacy, etc., etc.*

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FIRST THOUSAND.



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## PREFACE.

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THIS book is designed for the use of pharmacists, and especially as a text-book for students in pharmacy.

In the first portion of the book the author has attempted, in explaining the principles of volumetric analysis, to combine thoroughness with simplicity of expression.

*The United States Pharmacopœia* has been taken as the basis of the work, and the volumetric processes therein given are followed throughout, each step being carefully explained, and chemical equations inserted, wherever deemed necessary.

The author has also added descriptions of processes not given in the *Pharmacopœia*, but which are worthy of consideration.

In teaching volumetric analysis to students in pharmacy the author discovered the necessity for a work especially designed for this class of students.

Moreover, the requirements of the new edition of the *United States Pharmacopœia*, in which many volumetric processes are given, necessitate on the part of the careful pharmacist a knowledge of this branch of analytical chemistry; and no work that has as yet fallen into the hands of the author has seemed to be exactly suited to the needs of the practical pharmacist. Consequently the necessity for a book based upon the *Pharmacopœia* and free from technicality is apparent.

The latter portion of the book is devoted to descriptions of such special analytical processes as the pharmacist may be called upon to use, and such as are taught in the pharmaceutical colleges.

The author has selected such processes as can be easily and quickly executed, and has given the gravimetric only where volumetric processes cannot be employed.

In the subject-matter of the book little originality is claimed, but the author has used his own judgment in its selection and arrangement.

He has endeavored in the text to give credit wherever it was due, and especially acknowledges his indebtedness to the United States Pharmacopœia ; Sutton's Volumetric Analysis ; Bartley's, Simon's, and Attfield's text-books ; Blythe's Food Analysis ; Prescott's Organic Analysis ; Muter's Analytical Chemistry (*American edition*) ; Lefmann and Beam's Milk and Water Analysis ; and Witthaus' and Holland's Urine Analysis.

He wishes to express his thanks to Dr. J. F. Golding for the valued assistance he has rendered during the preparation of the book. He is also indebted to Richards & Co., of 41 Barclay Street, N. Y. City, manufacturers of chemical apparatus, from whom several of the cuts were borrowed.

The author submits this work to the consideration of pharmacists, trusting its reception will be at least commensurate with the labor expended in its preparation.

HENRY W. SCHIMPF.

365 FRANKLIN AVE., BROOKLYN, N. Y.

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A LIST OF ELEMENTS OCCURRING IN VOLUMETRIC  
METHODS, THEIR SYMBOLS, AND ATOMIC WEIGHTS.

Name.		Exact Atomic Weights according to Meyer and Seubert, adopted by the U. S. P.	Approximate Atomic Weights.
Albuminium.....	Al	27.04	27.0
Antimony.....	Sb	119.6	120.0
Arsenic.....	As	74.9	75.0
Barium.....	Ba	136.9	136.9
Bismuth.....	Bi	208.9	208.0
Boron.....	B	10.9	11.0
Bromine.....	Br	79.76	80.0
Cadmium.....	Cd	111.5	111.5
Calcium.....	Ca	39.91	40.0
Carbon.....	C	11.97	12.0
Chlorine.....	Cl	35.37	35.4
Chromium.....	Cr	52.0	52.0
Copper.....	Cu	62.18	63.0
Gold.....	Au	196.7	196.7
Hydrogen.....	H	1.0	1.0
Iodine.....	I	126.53	126.5
Iron.....	Fe	55.88	56.0
Lead.....	Pb	206.4	206.4
Lithium.....	Li	7.01	7.0
Magnesium.....	Mg	24.3	24.0
Manganese.....	Mn	54.8	55.0
Mercury.....	Hg	199.8	200.0
Nitrogen.....	N	14.01	14.0
Oxygen.....	O	15.96	16.0
Phosphorus.....	P	30.96	31.0
Platinum.....	Pt	194.3	194.3
Potassium.....	K	39.03	39.0
Silver.....	Ag	107.66	107.7
Sodium.....	Na	23.0	23.0
Strontium.....	Sr	87.3	87.3
Sulphur.....	S	31.98	32.0
Tin.....	Sn	118.8	118.0
Zinc.....	Zn	65.1	65.0

## ABBREVIATIONS AND SIGNS.

Cc . . . . . cubic centimetre.

Gm . . . . . gramme, 15.43235 grains.

Gr. . . . . grain.

At. wt . . . . atomic weight.

V. S . . . . . volumetric solution.

T. S . . . . . test solution, according to U. S. P.

U. S. P. . . . United States Pharmacopœia.

$\frac{N}{1}$  . . . . . normal.

$\frac{N}{10}$  . . . . . decinormal.

$\frac{N}{100}$  . . . . . centinormal.

$\frac{N}{2}$  . . . . . semi-normal.

$\frac{2}{N}$  or 2N . . double-normal.

\* means that the figure is approximate.

# A TEXT-BOOK OF VOLUMETRIC ANALYSIS.

---

## PART I. *INTRODUCTION.*

---

### CHAPTER I.

**1. Quantitative Analysis** is the determination of the proportions in which the constituents of a compound are present.

The quantitative analysis of a substance may be made by the *Gravimetric Method* or by the *Volumetric Method*.

**2. The Gravimetric Method** consists in separating and weighing the constituents, either in their natural state or in the form of some new and definite compounds the composition of which is known to the operator, and from their weights calculating the weights of the original constituents.

*For example:* A silver solution is treated with hy-

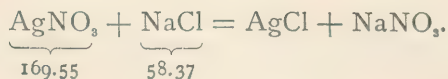
drochloric acid as long as a precipitate is produced. This precipitate is thoroughly washed, dried, and weighed. It consists of silver chloride 143.03 parts, which contain 107.66 parts (by weight) of metallic silver.

These operations are often very complicated, require great skill and elaborate apparatus, besides consuming considerable time.

**3. The Volumetric Method** is more easily performed. In this the quantity of the substance under examination is ascertained by a calculation based upon a measured quantity of a solution of known strength required to perform a certain reaction with it. For instance, if a silver solution is to be analyzed by this method, it is treated with a solution of sodium chloride of certain strength until no more silver chloride is precipitated.

The sodium-chloride solution used for this purpose is a  $\frac{N}{10}$  solution, and is made by dissolving one tenth of the molecular weight in grammes, in sufficient water to make one thousand cubic centimetres (1 litre).

As seen by the equation, one molecule of sodium chloride (58.37 parts by weight) will precipitate all the silver out of one molecule of silver nitrate (169.55 parts by weight).



Hence 1000 cc. of the  $\frac{N}{10}$  sodium-chloride solution represent 16.955 grammes of silver nitrate, and each cc. precipitates .016955 gramme.



Volumetric operations can be quickly performed, and with great accuracy.

The apparatus required is simple, and comparatively little skill is necessary. The volumetric method is therefore to be preferred to the gravimetric whenever it can be employed.

The solutions used are known as *volumetric* or *standard* solutions.

## CHAPTER II.

**4. Standard and Normal Solutions.**—When volumetric analysis first came into use the solutions were so made that each substance to be estimated had its own special volumetric solution, and this was generally of such strength as to give the result in percentages.

Thus a certain strength of solution was used for testing soda, another for potassa, and a third for ammonia.

These solutions were known as normal solutions, and since they are still to some extent in use it is important that no misconception should exist as to what a normal solution is. It is to be regretted that some authors define a normal solution as one having the molecular weight in grammes of the active reagent in a litre.

**5. A Normal Solution** is one which contains in a litre a quantity of the active reagent, expressed in grammes, and chemically equivalent to one atom of hydrogen.

**6. A Standard Solution** is any solution employed in volumetric analysis for the purpose of estimating the strength of substances—that is, any solution the strength or chemical power of which has been determined. It may be normal, decinormal, or of any strength so long as its strength is known. Such a solution is said to be “titrated” (French *titre* = title or power), sometimes called a “set” solution or “standardized” solution.

Standard solutions for use in volumetric analysis are usually solutions of acids, bases, or salts, and in two cases elements, namely, iodine and bromine.

A standard solution of a base is usually used for the estimation of free acids.

A standard solution of an acid is usually used for the estimation of a free base, or the basic part of a salt, the acid of which can be completely expelled by the acid used in the standard solution. Example, carbonates.

A standard solution of a salt may be used, as a precipitant, or it may be used as an oxidizing or reducing agent.

That part of the reagent in a standard solution which reacts with the substance under analysis is the active constituent of the solution. As Ag in  $\text{AgNO}_3$  is the active constituent of the standard solution of silver nitrate,



or Cl in NaCl, is the active constituent of the standard solution of sodium chloride.

If the reagent is a base, as KOH, the basic part K is the active constituent. If the reagent is an acid, the active constituent is the acidulous part, as  $\text{SO}_4$  in  $\text{H}_2\text{SO}_4$ .

If the action of the reagent is oxidizing, then that part of the reagent which produces the oxidation is the active constituent.

The valence of an acid is shown by the number of replaceable hydrogen atoms it contains. Thus, HCl is univalent,  $\text{H}_2\text{SO}_4$  is bivalent; which means that a molecule of HCl is chemically equivalent to one atom of

hydrogen, and a molecule of  $\text{H}_2\text{SO}_4$  is chemically equivalent to two atoms of hydrogen.

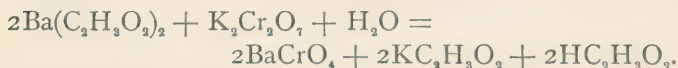
The valence of a base is shown by the number of hydroxyls it is combined with. As  $\text{KOH}$  is univalent,  $\text{Ca}(\text{OH})_2$  is bivalent.

The valence of a salt is shown by the equivalent of base which has replaced the hydrogen of the corresponding acid.

Thus  $\text{NaCl}$ , in which  $\text{Na}$  has replaced  $\text{H}$  of  $\text{HCl}$ , is univalent.

$\text{K}_2\text{SO}_4$ , in which  $\text{K}_2$  has replaced  $\text{H}_2$  of  $\text{H}_2\text{SO}_4$ , is bivalent.

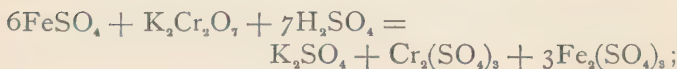
If a normal solution is to be made for a special purpose, its reaction in that special case is to be considered. As, when  $\text{K}_2\text{Cr}_2\text{O}_7$  is to be used as a precipitating agent its reaction is as follows:



It is thus seen that one molecule of  $\text{K}_2\text{Cr}_2\text{O}_7$  will cause the precipitation of two atoms of barium in the form of chromate. Each atom of barium is chemically equivalent to two atoms of hydrogen; therefore one fourth of a molecule of  $\text{K}_2\text{Cr}_2\text{O}_7$  is equivalent to one atom of hydrogen. And therefore a normal solution of this salt when used as a precipitating agent must contain in one litre one fourth of its molecular weight in grammes.

If  $\text{K}_2\text{Cr}_2\text{O}_7$  is to be used as an oxidizing agent, the three atoms of oxygen which it yields for oxidizing purposes must be taken into account. When this salt oxidizes it splits up into  $\text{K}_2\text{O} + \text{Cr}_2\text{O}_3 + \text{O}_3$ . The three atoms of oxygen combine with and oxidize the

salt acted upon, or they combine with an equivalent quantity of the hydrogen of an acid and liberate the acidulous part, which then combines with the salt. As the equations show,



Each of these atoms of oxygen are equivalent to two atoms of hydrogen. Thus  $\text{O}_3$  is equivalent to  $\text{H}_6$ .

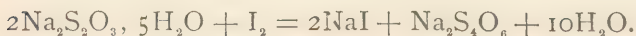
Hence a litre of a normal solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ , when used as an oxidizing agent, contains one sixth of its molecular weight in grammes.

The same may be said of potassium permanganate when used as an oxidizing agent.

$2\text{KMnO}_4$  has five atoms of oxygen which are available for oxidizing purposes, and each of these is capable of taking two atoms of hydrogen from an acid and liberating the acidulous part. The hydrogen equivalent of this salt may therefore be said to be one tenth of the weight of  $2\text{KMnO}_4$ , and a normal solution of this salt contains 31.534 gm. in a litre.

Sodium Thiosulphate (Hyposulphite),  $\text{Na}_2\text{S}_2\text{O}_3$ , is another instance. The molecule of this salt has two atoms of sodium, which have replaced two atoms of hydrogen of thiosulphuric acid. Thus it would seem that a normal solution should contain one half of the molecular weight in grammes. But the particular reaction of this salt with iodine is taken into account.

One molecule reacts with one atom of iodine, as seen by the equation



Since iodine is univalent, a molecule of the salt is equivalent to one atom of hydrogen.

A normal solution of this salt therefore contains the molecular weight in grammes in a litre.

According to the U. S. P., Normal solutions  $\left(\frac{N}{I}\right)$  are those which contain in one litre (1000 cc.) the molecular weight of the active reagent in grammes, and reduced to the valence corresponding to one atom of replaceable hydrogen or its equivalent.

Thus oxalic acid  $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} = 125.7$ , having two replaceable H atoms. One half of its molecular weight in grammes is contained in a litre of its normal solution, while hydrochloric acid  $\text{HCl} = 36.37$ , which has but one replaceable H atom, has its full molecular weight in grammes in a litre of its normal solution. Sulphuric acid  $\text{H}_2\text{SO}_4$  has two replaceable H atoms, so its normal solution contains one half of its molecular weight in grammes in a litre. NaOH and KOH being monobasic, a litre of a normal solution of either contains the full molecular weight of the salt in grammes.

**7. Decinormal Solutions,**  $\frac{N}{10}$ , are one tenth the strength of normal solutions.

**8. Centinormal Solutions,**  $\frac{N}{100}$ , are one hundredth the strength of normal solutions.



**9. Seminormal Solutions,**  $\frac{N}{2}$ , are one half the strength of normal solutions.

**10. Double-normal Solutions,**  $\frac{2}{N}$ , are twice the strength of the normal.

**11. Empirical Solutions** are those which do not contain an exact atomic proportion of reagent, but are generally of such strength that 1 cc. = 0.01 gm. of the substance upon which it acts.

**12. To Titrate** a substance means to test it volumetrically for the amount of pure substance it contains. The term is used in preference to "tested" or "analyzed," because these terms may relate to qualitative examinations as well as quantitative, whereas titration applies only to volumetric analysis.

**13. Residual Titration, Re-titration,** sometimes called Back Titration, consists in treating the substance under examination with standard solution in a quantity known to be in excess of that actually required; the excess (or residue) is then ascertained by residual titration with another standard solution.

Thus the quantity of the first solution which went into combination is found.

*Example.*—Ammonium carbonate is treated first with  $\frac{N}{I}$ -H<sub>2</sub>SO<sub>4</sub> in excess, and the excess then found by titration with  $\frac{N}{I}$  KOH.

The quantity of the  $\frac{N}{I}$ -KOH used is then deducted from the quantity of  $\frac{N}{I}$ -H<sub>2</sub>SO<sub>4</sub> added, which gives the quantity of the latter which was neutralized by the ammonium carbonate.

## CHAPTER III.

**An Indicator** is a substance which is used in volumetric analysis, and which indicates by change of color, or some other visible effect, the exact point at which a given reaction is complete.

Generally the indicator is added to the substance under examination, but in a few cases it is used alongside, a drop of the substance being occasionally brought in contact with a drop of the indicator.

Thus in estimating an alkali with an acid-volumetric solution the alkali is shown to be completely neutralized when the litmus tincture which was added becomes faintly red or the phenolphthalein colorless. Again, when haloid salts are estimated with nitrate-of-silver solution, chromate of potassium is added as indicator. A white precipitate is produced as long as any halogen is present to combine with the silver, and when all is precipitated the chromate of potassium acts upon the silver nitrate, forming the red-silver chromate, this color thus showing that all the halogen has been precipitated.

## INDICATORS.

The principal indicators used are :

**Tincture of Litmus**, which shows acidity by turning red and alkalinity by becoming blue.

**Phenolphthalein Solution**, which is colorless in acid solutions and red in alkaline solutions, but is not

reliable for alkaline phosphates, bicarbonates, or ammonia.

**Methyl-orange Solution** turns red with acids and yellow with alkalis. It is not affected by carbonic acid, and is therefore adapted for the titration of alkaline carbonates.

**Rosolic-acid Solution** is yellow with acids and violet-red with alkalis. It is very sensitive to ammonia.

**Tincture of Turmeric** turns brown with alkalis, and the yellow color is restored by acids.

**Cochineal Solution** turns violet with alkalis and yellowish with acids. It is used chiefly in the presence of ammonia or alkaline earths.

**Eosin Solution** is red by transmitted light, and shows a strong green fluorescence by reflected light. Acids destroy this fluorescence and alkalis restore it.

**Brazilwood Test-solution** turns purplish red with alkalis and yellow with acids.

**Fluorescein Test-solution** shows a strong green fluorescence by reflected light in the presence of the least excess of an alkali.

**Neutral Potassium-chromate Test-solution** is used in the titration of haloid salts with silver-nitrate solution. It indicates that all the halogen has combined with the silver by producing a red-colored precipitate (silver chromate).

**Potassium-ferricyanide Test-solution** is used in the estimation of ferrous salts with potassium-dichromate solution. It gives a blue color to a drop of the solution on a white slab as long as any iron salt is present which has not been oxidized to ferric.

Many other indicators are also used.

## CHAPTER IV.

## GENERAL PRINCIPLES OF CHEMICAL COMBINATION UPON WHICH VOLUMETRIC ANALYSIS IS BASED.

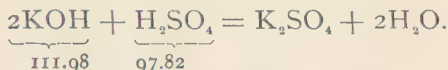
1. When substances unite chemically the union always takes place in definite and invariable proportions. Thus when silver nitrate and sodium chloride are brought together, 169.55 parts (by weight) of silver nitrate and 58.37 parts (by weight) of sodium chloride will react with each other, producing 143.05 parts of a curdy white precipitate (silver chloride).

These substances will react with each other in these proportions only.

If a greater proportion of silver nitrate than that above stated be added to the sodium chloride, only the above proportion will react, the excess remaining unchanged.

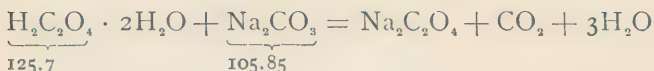
The same is true if sodium chloride be added in excess of the above proportions. For instance, if 200 parts of silver nitrate be mixed with 58.37 parts of sodium chloride 169.55 parts only will react with the sodium chloride, while 30.45 parts of silver nitrate will remain unchanged. Again, when potassium hydroxide and sulphuric acid are mixed potassium sulphate is formed, 111.98 parts of potassium hydroxide and 97.82 parts of sulphuric acid being required for complete neutralization. These two substances unite chemically in these proportions only.

The equation is



In other words, 111.98 parts of KOH will neutralize 97.82 parts of  $\text{H}_2\text{SO}_4$ , and consequently 97.82 parts of  $\text{H}_2\text{SO}_4$  will neutralize 111.98 parts of KOH.

Oxalic acid and sodium carbonate react upon each other in the proportions shown in the equation



125.7 parts of crystallized oxalic acid are neutralized by 105.85 parts of anhydrous sodium carbonate.

2. Definite chemical compounds always contain the same elements in exactly the same proportions, the proportions being those of their atomic weights, or some multiple of these weights.

Thus sodium chloride ( $\text{NaCl}$ ) contains 23 parts of metallic sodium and 35.37 parts of chlorine, these being the atomic weights of sodium and chlorine, respectively.

Potassium sulphate ( $\text{K}_2\text{SO}_4$ ) contains twice  $39.03 = 78.06$  parts of potassium, 31.98 parts of sulphur, and four times  $15.96 = 63.84$  parts of oxygen.

Potassium hydroxide ( $\text{KOH}$ ) contains 39.03 parts of potassium, 15.96 parts of oxygen, and one part of hydrogen. Hydrochloric acid ( $\text{HCl}$ ) contains one part of hydrogen and 35.37 parts of chlorine.

Upon these facts the volumetric methods of analysis are based.

It has been shown that 97.82 grammes of sulphuric acid will neutralize 111.98 grammes of potassium hy-

droxide ; it is therefore evident that if a solution of sulphuric acid be made containing 48.91 grammes of the pure acid in 1000 cc. that one cc. of this solution will neutralize 0.056 gm. of potassium hydroxide. In estimating alkalies with this acid solution the latter is added from a burette, in small portions, until the alkali is neutralized, as shown by its reaction with some indicator.

Each cc. of the acid solution required before neutralization is complete indicates 0.056 gm. of KOH, and the number of cc. used multiplied by 0.056 gm. gives the quantity of pure KOH in the sample analyzed.

One cc. of the same solution will neutralize 0.03996 gm. of sodium hydroxide (NaOH), 0.052925 gm. of anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), etc.

If a solution of crystallized oxalic acid be made by dissolving 62.85 gm. in sufficient water to make 1000 cc., we will have a normal solution, the neutralizing power of which is exactly equivalent to the above-mentioned normal sulphuric-acid solution.

The strength of acids is estimated by alkali volumetric solutions. A normal solution of potassium hydroxide containing 55.99 gm. in the litre will neutralize exactly 1 litre of the normal acid solution ; 1 cc. of this normal alkali will neutralize 0.03637 gm. of HCl, 0.06285 gm. of  $\text{H}_2\text{C}_2\text{O}_4$ , or 0.04891 gm. of  $\text{H}_2\text{SO}_4$ , etc.



## CHAPTER V.

## WEIGHTS AND MEASURES USED IN VOLUMETRIC ANALYSIS.

THE metric or decimal system is used in this country and on the continent in Europe, but in England the grain system is used.

The unit of weight in the metric system is the gramme (gm.).

A gramme of distilled water at its maximum density,  $4^{\circ}$  C. ( $39^{\circ}$  F.), measures one cubic centimetre (cc.).

A kilogram is 1000 gms.

A litre is 1000 cubic centimetres.

Volumetric instruments are graduated in the metric system, but not at  $4^{\circ}$  C. If they were, it would necessitate the carrying out of all volumetric operations at that temperature, and it would be impossible to do careful volumetric work except for two or three months of the year, unless troublesome calculations for the correction of volume were made.

For this reason the temperature of  $15^{\circ}$  C. ( $59^{\circ}$  F.) was taken as the standard, and at this temperature most volumetric instruments are graduated. In making very careful examinations the work should be done at this temperature.

One gramme of distilled water at  $15^{\circ}$  C. measures one cc. as used in volumetric analysis.

The true cc. weighs at  $15^{\circ}$  C. only 0.999 gm. Casa-major (C. N., xxxv. 160) gives the following figures,

showing the relative contraction and expansion of water below and above 15° C.:

Degree C.	Degree C.
8 — .000590	17 + .000305
9 — .000550	18 + .000473
10 — .000492	19 + .000652
11 — .000420	20 + .000841
12 — .000334	21 + .001039
13 — .000236	22 + .001246
14 — .000124	23 + .001462
15 — normal	24 + .001686
16 + .000147	25 + .001919

By means of these numbers it is easy to calculate the volume of liquid at 15° C. corresponding to any volume observed at any temperature between 8° C. and 25° C. If 25 cc. of solution had been used at 20° C., the table shows that 1 cc. of water passing from 15° to 20° is increased to 1.000841 cc. Therefore, by dividing 25 cc. by 1.000841, the quotient, 24.97 cc., is obtained, which represents the volume at 15° C. corresponding to 25 cc. at 20° C.

These corrections are of value only for very dilute solutions and for water, but useless for concentrated solutions. Slight variations of atmospheric pressure may be disregarded,

## CHAPTER VI.

## APPARATUS USED IN VOLUMETRIC ANALYSES.

**The Burette** is a graduated glass tube which holds from 25 to 100 cc. and is graduated in fifths or tenths of a cc., and provided at the lower end with a rubber tube and pinch-cock. The use of this instrument is to accurately measure quantities of standard solutions used in an analysis. It is in an upright position when in use, and the flow of the solution can be regulated so as to run out in a stream or flow in drops by pressing the pinch-cock between the thumb and forefinger. The quantity of solution used can be read from the graduation on the outside of the tube. This is the simplest and most common form of burette, and is known as *Mohr's* (Fig. 1).

The greatest drawback to this burette is that it cannot be used for permanganate or other solutions that act upon the rubber.

This defect can be overcome by the use of a burette having a glass stop-cock in place of the rubber tubing and pinch-cock. This form has the additional advantage of being capable of delivering the solution in



FIG. 1.

drops while both hands of the operator are disengaged (Fig. 2).

Another good arrangement is that in which the tap



FIG. 2.



FIG. 3.

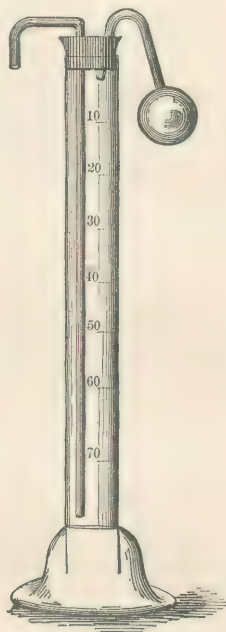


FIG. 4.

is placed in an oblique position, so that it will not easily drop out of place (Fig. 3).

These glass stop-cock burettes should be emptied and washed immediately after use, especially if soda or potassa solution has been used; for these act upon the glass, and often cause the stopper to stick so firmly that it cannot be turned or removed without danger of breaking the instrument.

Other forms of burettes are *Mohr's Foot Burette*,

with rubber ball (Fig. 4). There is a hole in the rubber ball, and by placing the thumb over the hole and gently squeezing, the flow of the liquid may be nicely regulated.

*Bink's Burette* (Fig. 5) is used by holding in the



FIG. 5.

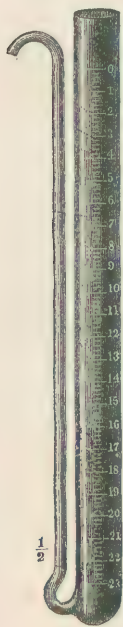


FIG. 6.



FIG 6a.

hand and inclining sufficiently to allow the liquid to flow, then placing in an upright position, and reading when the surface of the liquid has settled.

*Gay-Lussac's* (Fig. 6) must also be inclined when used. A wooden foot is generally provided, into

which this burette is placed to rest in an upright position. By inserting a tightly-fitting cork into the open end and passing through this cork a small bent glass tube, the flow of the solution from the exit-tube can be nicely regulated by blowing through the small glass tube. The necessity for inclining the burette is thus obviated. See Fig. 6a.

These two latter burettes being held in the hand when in use, there is a chance of increasing the bulk of the fluid by the heat of the body, thus leading to incorrect measurements.

The use of the pinch-cock in Mohr's burette may be dispensed with by introducing into the rubber tube a small piece of glass rod, which must not fit too tightly. By firmly squeezing the rubber tube surrounding the glass rod a small canal is opened, through which the liquid escapes. A very delicate action can in this way be obtained, and the flow of the liquid is completely under the control of the operator. (See Fig. 7.)

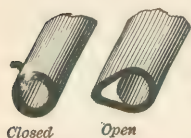


FIG. 7.

**The Measuring-flask** is a vessel made of thin glass having a narrow neck, and so constructed as to hold a definite amount of liquid when filled up to the mark on the neck. These flasks are of various sizes, holding 100, 250, 500, 1000 cc., etc., but are generally called "*Litre Flasks.*" (Fig. 8).

They are used for making volumetric solutions.

Those which have the mark below the middle of the neck are to be preferred, because the contents can be more easily shaken.

**The Test Mixer, or Graduated Cylinder** (Fig. 9), is for measuring and mixing smaller quantities of solutions.

They are made of different sizes, holding 100, 250, 500, and 1000 cc., and graduated in fifths or tenths of a cc.



FIG. 8.

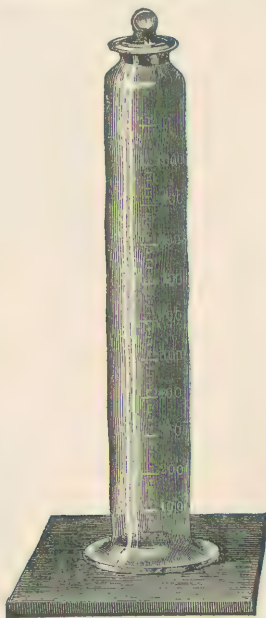


FIG. 9.

**Pipettes** are of two kinds: those which are marked for one quantity only, and those which are graduated on the stem to deliver various quantities (Fig. 10 and Fig. 10a). Pipettes are filled by applying the mouth to the upper end and sucking the liquid up to the mark; then by placing the moistened forefinger over the upper opening the liquid is prevented from running out, but may be delivered in drops or allowed to run out to any mark by loosening the finger.

A very convenient form of pipette is one which has attached to its upper end a piece of rubber tubing, into which a piece of glass rod has been inserted.



By squeezing the rubber surrounding the glass rod firmly between the fingers a canal is opened, and the liquid can be drawn up into the pipette by suction with the lips. Then by gentle pressure the liquid can be allowed to run out slowly, and stopped at any point by removing the pressure (Fig. 11).

*The Nipple Pipette* is very convenient for measur-

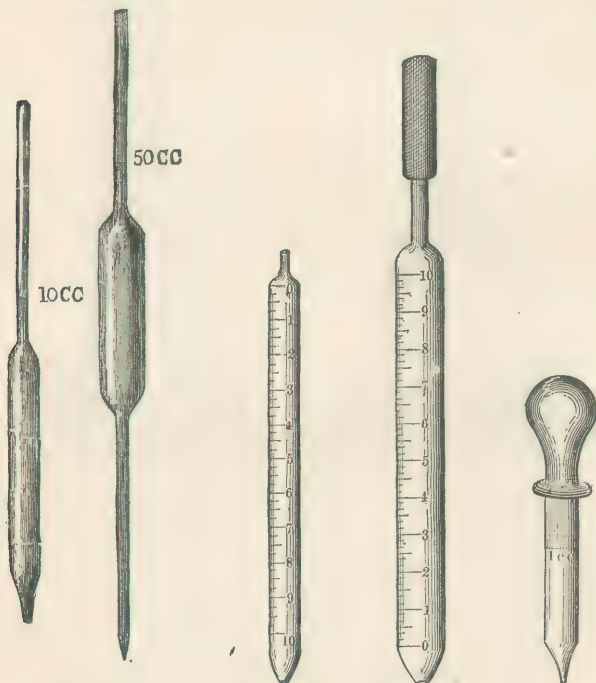


FIG. 10.

FIG. 10a.

FIG. 11.

FIG. 12.

ing small quantities of liquids, such as 1 or 2 cc. (Fig. 12).

When a volatile or highly poisonous solution is to be measured it is not advisable to suck it up with the mouth. The pipette may then be filled by dipping it

into the liquid contained in a long, narrow vessel until the liquid reaches the proper mark on the pipette, then closing the upper opening and withdrawing.

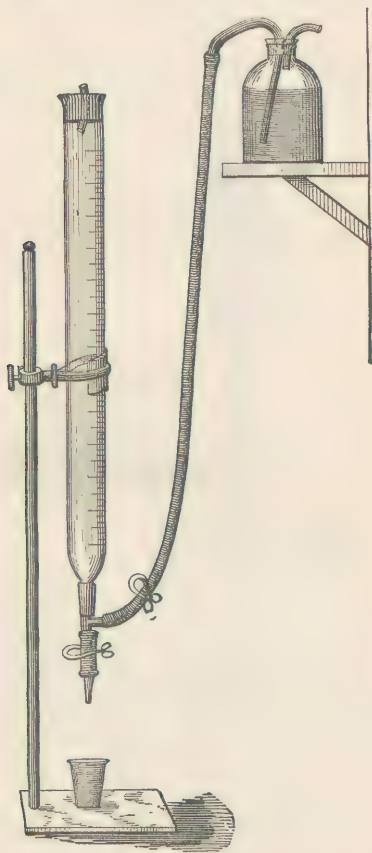


FIG. 13.

When this is done the liquid which adheres to the outside of the pipette should be dried off before the measured liquid is delivered.

When a number of estimations are to be made in which the same volumetric solution is employed, the arrangement shown in Figs. 13 and 14 is very serviceable.

A T-shaped glass tube is inserted between the lower end of the burette and the pinch-cock and connected

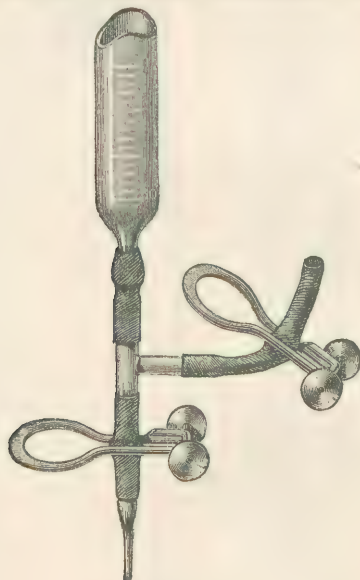


FIG. 14.

by a rubber tube with a reservoir containing the volumetric solution. The tube which communicates with the reservoir is provided with a pinch-cock, which when open allows the solution to flow into and fill the burette in so gradual a manner that no bubbles are formed. The burette is emptied in the usual manner.

If the titration is to be conducted at a high temperature, as in the estimation of carbonates, when litmus is used as the indicator, or in the estimation of sugar

by copper solution, a long rubber tube should be attached to the lower end of the burette. The boiling can then be done at a little distance, and the expansion



FIG. 15.

of the liquid in the burette avoided. The pinch-cock is fixed about midway on the tube.

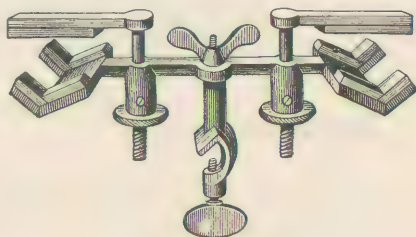


FIG. 16.

The burette support represented in Fig. 15, with heavy tripod base, is one of the best for one or two

burettes. It stands firmly upon an uneven surface, and does not easily tip over.

If two burettes are to be supported the clamp shown

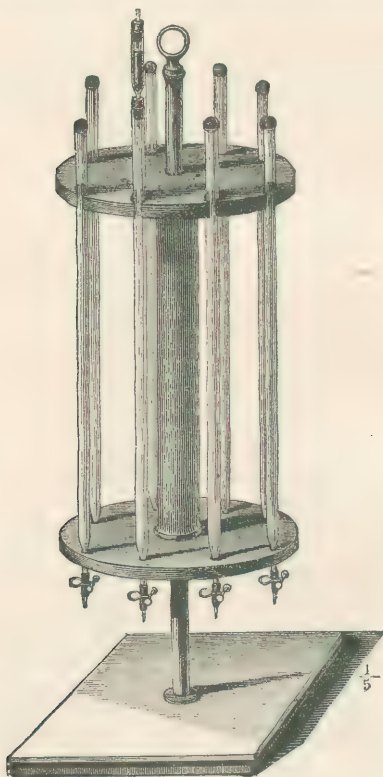


FIG. 17.

in Fig. 16 may be used. Fig. 17 represents a revolving burette-holder for eight burettes.

## CHAPTER VII.

## ON THE USE OF APPARATUS.

It is important that all apparatus used in volumetric analysis should be perfectly clean. Even new apparatus should be cleansed by passing dilute hydrochloric acid through them and then rinsing with distilled water.

If the burette, pipette, or other instrument is even slightly greasy, the liquid will not flow smoothly, and drops of the liquid will remain adhering to the sides, thus leading to inaccurate results.

Greasiness may be removed with dilute soda solution. If this fails the instrument should be allowed to remain for some little time in a solution containing sulphuric acid and potassium dichromate, which will radically remove all traces of grease.

The burette or other measuring instruments should never be filled with volumetric solution without first rinsing, even if the burette be perfectly dry.

It is well to wash the inside of the instrument with two or three small portions of the solution with which it is to be filled.

The burette may be filled with the aid of a funnel, the stem of which should be placed against the inner wall of the burette so that the solution will flow down the side and thus prevent the formation of bubbles.

The burette should be filled to above the zero mark,

and the air-bubbles, if there are any, removed by gently tapping with the finger.

A portion of the liquid should then be allowed to run out in a stream so that no air-bubbles remain in the lower part of the burette. In the glass tap burette it can be easily seen if any air is present, but in the pinch-cock burette it is sometimes necessary to take hold of the rubber tube between the thumb and forefinger and gently stroke upward. Or the glass nip at the lower end of the burette may be pointed upward, and the pinch-cock opened wide so that a stream of the liquid will pass through and force out any air that may be inclosed.

#### ON THE READING OF INSTRUMENTS.

In narrow vessels the surfaces of liquids are never level. This is owing to the capillary attraction exerted by the sides of the vessel upon the liquid, drawing the edge up and forming a saucerlike concavity (Fig. 18). All liquids present this concave surface except mercury, the surface of which is convex.



FIG. 18.

This behavior of liquids makes it difficult to find a distinct level, and in reading the measure either the upper meniscus (*a*) or the lower meniscus (*b*) may be used (Fig. 19).

The most satisfactory results are obtained if the lowest point of the curve (*b*) is used, especially with light-colored solutions. But if dark-colored or opaque solutions are measured, it is necessary to use the upper meniscus (*a*) for reading.

In all cases the eye should be brought on a level



with the surface of the liquid in reading the graduation.

The eye is very much assisted by using a small card, the lower half of which is black and the upper half white. This card is held behind the burette, the dividing line between white and black being about an eighth of an inch below the surface of the liquid. The

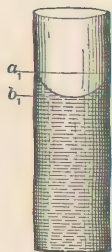


FIG. 19.

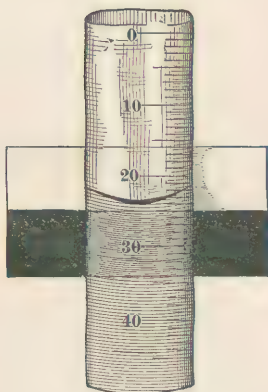


FIG. 20.



FIG. 21.

eye is then brought on a level with it, and the lower meniscus can be distinctly seen as a sharply-defined black line against the white background (Fig. 20).

**Erdman's Float**, Fig. 21, is an elongated glass bulb, which is weighted at its lower end with mercury, to keep it in an upright position when floating. It is of such diameter that it will slide easily up and down

inside of a burette. There is a ring at the top by which it can be lifted in or out by means of a bent wire. Around its centre a line is marked. At this line instead of at the meniscus the reading is taken.

These floats are sometimes provided with a thermometer, and they then register the temperature as well as the volume.

Litre flasks are sometimes made with two marks on the neck very near together; the lower one is the litre-mark. If the flask is required to deliver a litre, it must be filled to the upper mark; the difference between the two measures being the equivalent of the liquid which remains in the flask, adhering to the sides.

## CHAPTER VIII.

## METHODS OF CALCULATING RESULTS.

EACH cc. of a  $\frac{N}{I}$  univalent volumetric solution contains  $\frac{1}{1000}$  of the molecular weight in grammes of its reagent, and will neutralize  $\frac{1}{1000}$  of the molecular weight of a univalent substance, or  $\frac{1}{2000}$  of the molecular weight of a bivalent substance.

Each cc. of a  $\frac{N}{I}$  bivalent volumetric solution contains  $\frac{1}{2000}$  of the molecular weight in grammes of its reagent, and will neutralize or combine with  $\frac{1}{2000}$  of the molecular weight of a bivalent salt, or  $\frac{1}{1000}$  of the molecular weight of a univalent salt.

A  $\frac{N}{10}$  is only  $\frac{1}{10}$  the strength of a normal solution and will neutralize only  $\frac{1}{10}$  the quantity of salt, etc.

Normal and decinormal solutions of acids should neutralize normal and decinormal solutions of alkalis, volume for volume. Decinormal solution of silver nitrate and decinormal solution of hydrochloric acid or sodium chloride should combine volume for volume, etc.

**The Rules for Obtaining the Percentage** of pure substance in any commercial article, such as acids, alkalis, and various salts, are ;

1. With normal solutions  $\frac{1}{10}$  or  $\frac{1}{20}$  (according to its atomicity) of the molecular weight in grammes of the substance is weighed for titration, and the number of cc. of the V. S. required to produce the desired reaction is the percentage of the substance whose molecular weight has been used.

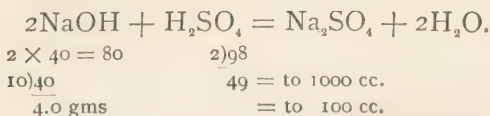
Thus, if sodium hydroxide (NaOH) is to be examined by titration with a normal acid solution  $\frac{1}{10}$  of its molecular weight in grammes, 4 gms. is weighed out, and each cc. of the acid solution required represents 1% of the pure salt.

If sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is to be tritated  $\frac{1}{20}$  of its molecular weight in grammes, 5.3 gms. is taken.

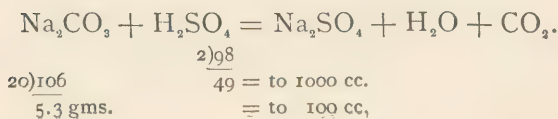
2. With decinormal solutions  $\frac{1}{100}$  or  $\frac{1}{200}$  of the molecular weight in grammes of the substance to be analyzed is taken, and the number of cc. will, in like manner, give the percentage.

The following equations will serve to explain more fully:

*Sodium hydroxide with  $\frac{N}{1}$  sulphuric acid:*



*Sodium carbonate with  $\frac{N}{1}$  sulphuric acid:*



With  $\frac{N}{10}$  sulphuric acid:



$$\begin{array}{rcl} 2 \times 40 = 80 & 2)98 & \\ 100)40 & 49 & = \text{to } 1000 \text{ cc.} \\ 0.40 \text{ gms.} & & = \text{to } 100 \text{ cc.} \end{array}$$

3. *Factors or coefficients for calculating the analyses.*—It frequently occurs that from the nature of the substance, or from its being in solution, this percentage method cannot be conveniently followed.

The best way to proceed in such a case is to find the factor.

The first step in all cases is to write the equation for the reaction which takes place between the substance under analysis and the solution used.

For instance, a solution of caustic potash is to be examined, a  $\frac{N}{1}$  solution of sulphuric acid being used.



$$\begin{array}{rcl} 2)112 & 2)98 & \\ 56 & 49 & = \text{to } 1000 \text{ cc. } \frac{N}{1} \text{ acid.} \\ 0.56 \text{ gm.} & .049 & = \text{to } 1 \text{ cc. } \frac{N}{1} \text{ acid.} \end{array}$$

The factor for KOH when  $\frac{N}{1}$  solution is used is .056 gm., that being the quantity neutralized by each cc. of the  $\frac{N}{1}$  acid. If  $\frac{N}{10}$  acid were used the factor would be .0056 gm.

The number of cc. of the acid used to produce the desired result, when multiplied by the factor gives the quantity in grammes of KOH in the solution taken.

*Example.*—If 10 grammes of caustic-potash solution were taken, and 40 cc. of  $\frac{N}{I}$  acid were required, the 10 gms. of solution contained .056 gm.  $\times 40 = 2.24$  gms. of pure KOH.

To find the percentage, the following formula may be used.

$$\frac{Q \times 100}{W} = \%.$$

$Q$  = the quantity of pure substance found by calculation;

$W$  = weight of substance taken.

If the above example is taken, we have

$$\frac{2.24 \times 100}{10} = 22.4\%.$$

Or the calculation may be made by proportion.

The quantity of the substance taken is always the first term, and the quantity of pure substance found, the second term.

The following rule is easily remembered: *As the quantity taken is to the quantity found, so is 100 to  $x$ , the percentage of pure substance in the sample.*

Three terms of the equation being given, the fourth is found by multiplying the means and dividing the product by the given extreme. By applying this rule to the above case we have

$$10 : 2.24 :: 100 : x, \quad x = 22.4\%.$$

TABLE SHOWING THE APPROXIMATE NORMAL FACTORS, ETC., OF THE ALKALIES, ALKALINE EARTHS, AND ACIDS.

Substance.	Formula.	Molecular Weight.	Normal Factor.*
Sodium hydroxide.....	NaOH	40	0.040
Sodium carbonate.....	Na <sub>2</sub> CO <sub>3</sub>	106	0.053
Sodium bicarbonate.....	NaHCO <sub>3</sub>	84	0.084
Potassium hydroxide.....	KOH	56	0.056
Potassium carbonate.....	K <sub>2</sub> CO <sub>3</sub>	138	0.069
Potassium bicarbonate.....	KHCO <sub>3</sub>	100	0.100
Ammonia (gas).....	NH <sub>3</sub>	17	0.017
Ammonium carbonate, normal. ...	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	96	0.048
Ammonium carbonate, commercial..	N <sub>3</sub> H <sub>11</sub> C <sub>2</sub> O <sub>5</sub>	157	0.052½
Lime.....	CaO	56	0.028
Calcium hydroxide.....	Ca(OH) <sub>2</sub>	74	0.037
Calcium carbonate.....	CaCO <sub>3</sub>	100	0.050
Nitric acid.....	HNO <sub>3</sub>	63	0.063
Hydrochloric acid ...	HCl	36.4	0.0364
Sulphuric acid.....	H <sub>2</sub> SO <sub>4</sub>	98	0.049
Oxalic acid, crystallized.....	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .2H <sub>2</sub> O	126	0.063
Acetic acid.....	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	60	0.060

\* This is the coefficient by which the number of cc. of normal solution used is to be multiplied in order to obtain the quantity of pure substance present in the material examined.



## CHAPTER IX.

## ANALYSIS BY NEUTRALIZATION.

THIS is based upon the fact that acids are neutralized by alkalis and alkalis by acids.

The strength of an acid is estimated by the quantity of alkali that is required to neutralize it. This process is called *acidimetry*.

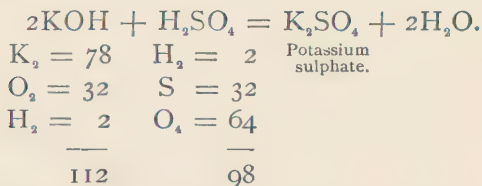
The strength of an alkali is found by the quantity of an acid that is required to neutralize it. This process is called *alkalimetry*. The stronger the acid, the more alkali is required, and *vice versa*.

A substance is said to be *alkaline* when it turns red litmus blue; phenolphthalein, red; turmeric, brown; etc. *Acid*, when it turns blue litmus red; red phenolphthalein, colorless, etc.

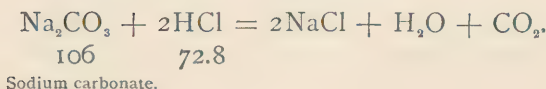
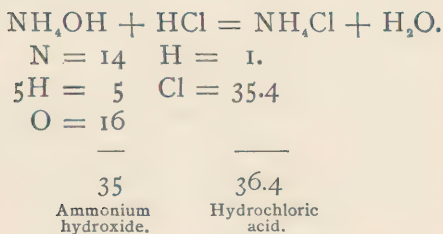
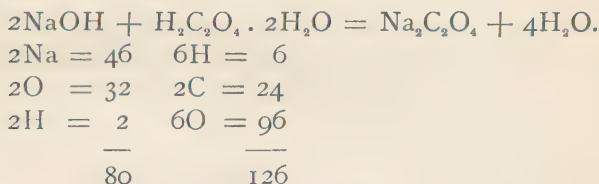
The principal alkaline substances are the hydroxides and carbonates of sodium, potassium, and ammonium, and the hydroxides and oxides of calcium, barium, and strontium, and the alkaloids.

When an acid is brought in contact with an alkali combination takes place, and a neutral salt is formed. This combination takes place in definite and invariable proportions; thus: If 112 parts of potassium hydroxide are mixed with 98 parts of absolute sulphuric acid the alkali as well as the acid will be neutralized. If only 80 parts of the acid have been added the mixture would still be alkaline, for it requires 98 parts of the

acid to neutralize it. If more than 98 of the acid have been added the mixture would consist of potassium sulphate and free sulphuric acid. The reaction is thus illustrated :



Sodium hydroxide will unite with oxalic, and form a neutral compound in the proportion of 80 parts by weight of the former and 126 parts by weight of the latter, as the equation shows :



Upon a careful perusal of the foregoing equations it will be seen that since definite weights of acids neutralize definite weights of alkalies the quantity of a certain alkali in solution can be easily determined by the quantity of an acid solution of known strength required to neutralize it, and *vice versa*.

If we make a solution of oxalic acid of such strength that 1000 cc. of it contains 63 gms. of the crystallized acid, 1 cc. of it will neutralize .056 gm. of KOH, .040 gm. of NaOH, or .035 gm. of  $\text{NH}_4\text{OH}$ .

Thus if 10 gms. of solution of KOH be treated with this oxalic-acid solution and it is found that 25 cc. of it are required to neutralize the alkali, the alkali solution contains  $25 \times .056 = 1.4$  gms. of pure KOH.

Since the acid and alkali as well as the neutral salt which is formed are colorless, and no visible change takes place during the reaction, it is necessary to add some substance which by change of color will show when the neutralization is complete. Such substances are known as indicators. A number of these are spoken of on page 10.

Neutralization is sometimes called saturation.

#### ALKALIMETRY.

**Preparation of Acid Volumetric Solutions.**—It is possible to carry out the titration of most alkalies with only one standard acid solution, but the standard acids are frequently required in other processes besides mere saturation, and it is therefore advisable to have a variety.

The standard oxalic acid is preferred by some because of the ease with which it may be prepared, pro-

vided a pure acid can be had. It does not, however, keep very long, and when used for titrating carbonates with methyl orange as an indicator the end reaction is not very distinct. Oxalic acid cannot very well be used for the titration of alkaline earths, since it forms insoluble compounds with these metals.

Sulphuric acid V. S. is preferred by others. A pure acid can be gotten without difficulty, and the standard solution made with it is totally unaffected by boiling, which cannot be said of either nitric or hydrochloric acid. Sulphuric acid, however, forms with alkaline earths insoluble compounds. For this reason standard solution of hydrochloric acid must frequently be employed.

**Normal Oxalic Acid V. S., U. S. P.**— $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} = 125.7 \cdot \left. \begin{matrix} 62.85 \\ *63. \end{matrix} \right\}$  gms. in 1 litre.

Dissolve 62.85 gms. (\*63 gms.) of pure oxalic acid (see below) in enough water to make, at or near  $15^\circ \text{C}$ ., exactly 1000 cc.

Pure oxalic acid, crystallized, is in the form of colorless, transparent, clinorhombic crystals, which should leave no residue when ignited upon platinum foil. It is completely soluble in 14 parts of water at  $15^\circ \text{C}$ . If the acid leaves a residue on ignition it should be purified by recrystallization, as directed by the U. S. P.

1 cc. of  $\frac{\text{N}}{\text{I}}$  oxalic acid V. S. is the equivalent of—

NaOH.....	0.03996 gm.
KOH.....	0.05599 “
NH <sub>3</sub> .....	0.01701 “

**Decinormal Oxalic Acid V. S., U. S. P.**— $\text{H}_2\text{C}_2\text{O}_4$   
 $+ 2\text{H}_2\text{O} = 125.7.$   $\left. \begin{array}{l} 6.285 \\ *6.3 \end{array} \right\}$  gms. in 1 litre.

Dissolve 6.285 gms. (\*6.3 gms.) of pure oxalic acid in enough water to make, at or near  $15^\circ \text{C}$ ., exactly 1000 cc.

1 cc. of  $\frac{\text{N}}{10}$  oxalic acid V. S. is the equivalent of—

$\text{NH}_3$ .....	0.001701 gm.
$\text{KOH}$ .....	0.005599 “
$\text{NaOH}$ .....	0.003996 “

**Normal Hydrochloric Acid V. S., U. S. P.**—  
 $\text{HCl} = 36.37.$   $\left. \begin{array}{l} 36.37 \\ 36.4 \end{array} \right\}$  gms. in 1 litre.

Mix 130 cc. of hydrochloric acid of sp. gr. 1.163, with enough water to measure, at or near  $15^\circ \text{C}$ ., 1000 cc.

Of this liquid (which is still too concentrated) measure carefully into a flask 10 cc., add a few drops of phenolphthalein T. S., and gradually add from a burette  $\frac{\text{N}}{1}$  potassium hydroxide V. S. until a permanent pale

pink tint is produced. Note the number of cc. of  $\frac{\text{N}}{1}$  potassium-hydroxide solution consumed, and then dilute the acid so that equal volumes of this and the  $\frac{\text{N}}{1}$   $\text{KOH}$  V. S. neutralize each other.

*Example.*—Assuming that the 10 cc. of the acid solution required 12 cc. of the  $\frac{\text{N}}{1}$   $\text{KOH}$ , each 10 cc. of

the acid must be diluted to 12 cc., or the whole of the remaining acid in the same proportion.

After the dilution a new trial should be made. 10 cc. of the acid V. S. should require exactly 10 cc. of the alkali.

This solution is exactly equivalent in neutralizing power to  $\frac{N}{I}$  oxalic acid V.S.

**Normal Sulphuric Acid V. S., U. S. P.**— $H_2SO_4 = 97.82$ .  $\left. \begin{array}{l} 48.91 \\ *49. \end{array} \right\}$  gms. in 1 litre.

Mix carefully 30 cc. of pure concentrated sulphuric acid (sp. gr. 1.835) with enough water to make about 1050 cc., and allow the liquid to cool to about 15° C.

Titrate 10 cc. of this liquid in the manner described under  $\frac{N}{I}$  hydrochloric acid, and dilute it so that equal volumes of the acid and the alkali will neutralize each other.

*Note.*—It is recommended in the U. S. P. that when a normal acid solution is required the normal sulphuric acid should be employed in place of  $\frac{N}{I}$  oxalic.

The oxalic-acid solution has a tendency to crystallize on the point of the burette.

**Decinormal Sulphuric Acid V. S., U. S. P.**— $H_2SO_4 = 97.82$ .  $\left. \begin{array}{l} 4.891 \\ 4.9 \end{array} \right\}$  gms. in a litre.

Dilute 10 cc. of the normal sulphuric-acid solution with enough water to make 100 cc.

The standardization of normal acid solutions may

also be effected by the use of pure anhydrous sodium carbonate.

Pure anhydrous sodium carbonate may be obtained by heating to dull redness a few grammes of *pure* sodium bicarbonate for about 15 minutes. The resulting carbonate is practically free from impurity.

The sodium bicarbonate loses on ignition one half of its carbonic acid gas:



The bicarbonate should, however, be tested before igniting, and if more than traces of chloride, sulphate, or thiosulphate are found, these may be removed by washing a few hundred grammes, first with a saturated solution of sodium bicarbonate, and afterward with distilled water.

0.53 gm. of the pure anhydrous sodium carbonate is accurately weighed and dissolved in about 20 cc. of water in a flask and a few drops of methyl orange T. S. added as indicator. The acid to be "set" or "standardized" is then run into the sodium-carbonate solution until a permanent light-red color is produced. It should require exactly 10 cc. of the  $\frac{N}{1}$  acid solution.

If 8 cc. of the acid solution are consumed to bring about the required result, then every 8 cc. must be diluted to 10 cc., or the whole of the remaining solution must be diluted in this proportion:



2)106	2)98	
53 gms.	49	= to 1000 cc. $\frac{N}{1}$ V. S.;
0.53 gm.		= to 10 cc. $\frac{N}{1}$



Instead of methyl orange, litmus tincture may be used. The carbonic-acid gas which is liberated in this reaction turns litmus red; the contents of the flask should therefore be boiled for a few minutes to drive off the  $\text{CO}_2$ , when the blue color will return. More acid is then run in until the mixture after boiling remains of a neutral color; indicating that just enough acid has been added to complete the reaction expressed in the foregoing equation.

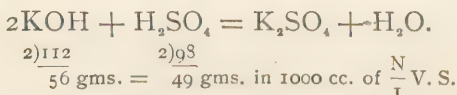
#### ESTIMATION OF ALKALINE HYDROXIDES.

A definite quantity of the substance is taken (generally weighed), and diluted with or dissolved in a little water in a flask or beaker. A few drops of a suitable indicator are now added, and the standard acid solution allowed to flow in until the last drop added just causes the color to change, the flask being agitated after each addition of the acid solution.

**Potassa.**  $\text{KOH} = \frac{55.99}{56}$  U. S. P.—Weigh carefully 1 gm. of potassa, dissolve it in a small quantity of water, add a drop of phenolphthalein solution as indicator, and titrate with  $\frac{N}{I}$  sulphuric acid V. S. until the red color just disappears. Each cc. of the normal acid solution used represents .056 gm. of pure potassa. To find percentage, multiply the factor (.056) by the number of cc. of  $\frac{N}{I}$  V. S. used, and then multiply the product by 100. Potassium hydroxide having great affinity for carbonic-acid gas, which it absorbs out of the air, generally contains small quantities of carbonate. There-

fore in titrating as above described it should be boiled once or twice toward the end of the reaction in order to drive off any  $\text{CO}_2$  which may be present. This gas, which has an acid reaction with phenolphthalein, would otherwise cause an incorrect estimation. This precaution should be taken with the other alkaline hydroxides.

The U. S. P. requirement is that 0.56 gm. of potassa be neutralized by not less than 9 cc. of the normal acid solution, each cc. corresponding to 10 per cent of pure potassium hydroxide. The equation is



This shows that 56 gms. of KOH are neutralized by 1000 cc. of  $\frac{\text{N}}{\text{I}}$  V. S.

Each cc. of this solution will therefore neutralize 0.056 gm. of KOH.

**Liquor Potassa, U. S. P.**—This is an aqueous solution of potassium hydroxide (KOH) containing about 5 per cent of the hydroxide.

It is estimated volumetrically in the same manner as potassa, 10 gms. of the solution of potassa being taken, each cc. of the  $\frac{\text{N}}{\text{I}}$  V. S. representing 0.056 gm. of KOH.

By multiplying the factor by the number of cc. of  $\frac{\text{N}}{\text{I}}$  V. S. used, the quantity of absolute KOH in the 10 gms. of liquor taken is obtained.

The percentage is then found by multiplying the quantity so obtained by 100 and dividing by the number of grammes of the liquor taken.

Thus if 9 cc. of the  $\frac{N}{I}$  V. S. were used, the 10 gms. taken contained  $9 \times 0.056 = 0.504$  gm. Then

$$10 \text{ gms.} : 0.504 :: 100 : x. \quad x = 5.04\%.$$

28 gms. of the U. S. P. liquor potassa should require about 25 cc. of the  $\frac{N}{I}$  acid V. S., each cc. representing 0.2% of KOH.

**Soda, (NaOH  $\left\{ \begin{smallmatrix} 39 \\ 40 \end{smallmatrix} \right.$  U. S. P.).**—1 gm. of soda is carefully weighed, dissolved in a small quantity of water, a few drops of phenolphthalein added, and then titrated with normal sulphuric acid V. S. until the red color of the indicator is just discharged. This equation shows the reaction :



$$\begin{array}{r} 2)80 \\ \hline 40 \text{ gms.} \end{array} = \begin{array}{r} 2)98 \\ \hline 49 \text{ gms.} \end{array} \text{ or } 1000 \text{ cc. of } \frac{N}{I} \text{ V. S.}$$

Thus each cc. represents 0.040 gm. of NaOH. 1 gm. should require 22.5 cc. of  $\frac{N}{I}$  acid V. S., which indicates 90%.

$$.040 \times 22.5 = .900$$

$$\frac{.900 \times 100}{I} = 90\%$$

**Liquor Soda, U. S. P.**—This is an aqueous solution, containing about 5% of the hydroxide (NaOH). 10 grammes of liquor soda are taken mixed with a little water, a few drops of phenolphthalein are added, and then from a burette the  $\frac{N}{I}$  sulphuric acid V. S. in the

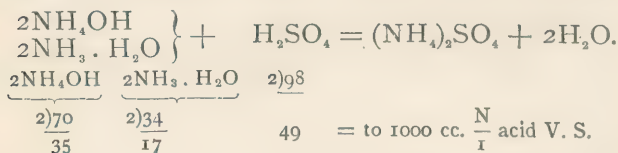
manner described above. Each cc. required represents 0.040 gm. of NaOH. If 12.5 cc. were required, then  $0.040 \times 12.5 = .500$ .

$$\frac{.500 \times 100}{10} = 5\%$$

**Aqua Ammoniae, U. S. P.**—An aqueous solution of ammonia ( $\text{NH}_3 = 17.01$ ) containing 10% by weight of the gas.

Three grammes of ammonia water are diluted with a little water, a few drops of rosolic acid T. S. are added, and then  $\frac{N}{I}$  sulphuric acid V. S. slowly from a burette until the yellow color indicates that all the alkali is neutralized. Phenolphthalein is not suitable as an indicator for ammonia. Litmus may be used, but it is not as delicate an indicator as rosolic acid.

Each cc. of  $\frac{N}{I}$  acid V. S. used represents 0.017 gm.  $\text{NH}_3$  or \*0.035 gm.  $\text{NH}_4\text{OH}$ , as shown by the equation



If the 3 gms. required 17.8 cc.  $\frac{N}{I}$  acid V. S., then it contained  $17.8 \times .017 \text{ gm.} = 0.3026 \text{ gm.}$

$$\frac{.3026 \times 100}{3} = 10.08\% \text{ of } \text{NH}_3.$$

According to the U. S. P., 3.4 gms. should require 20 cc. of normal acid V. S.

**Aqua Ammonia Fortior, U. S. P.** (Stronger Ammonia Water).—An aqueous solution of ammonia ( $\text{NH}_3$ ) containing about 28% by weight of the gas. This is estimated in the same manner as aqua ammonia, two grammes of the stronger ammonia water being taken instead of three.

**Spiritus Ammoniaë** (Spirit of Ammonia).—This is an alcoholic solution of  $\text{NH}_3$ , containing 10% by weight of the gas.

3.4 grammes (or 4.2 cc.) of the spirit are diluted with water and treated with  $\frac{\text{N}}{\text{I}}$  sulphuric V. S. Each cc. of the  $\frac{\text{N}}{\text{I}}$  acid solution used represents .017 gm. of  $\text{NH}_3$ , or 0.5%. 20 cc. should be required. Rosolic acid is the indicator.

#### ESTIMATION OF ALKALINE CARBONATES.

When carbonates are treated with acids carbonic-acid gas is liberated. This gas shows an acid reaction with most indicators, and the reaction will seem to be completed before the alkali is entirely neutralized. To avoid this the process is conducted at a boiling temperature in order to drive off the  $\text{CO}_2$ . The standard acid being added until two minutes' boiling fails to restore the color indicating alkalinity. If the titration is conducted at a boiling temperature it is advisable to attach to the lower end of the burette a long rubber tube with a pinch-cock fixed about midway on the tube.

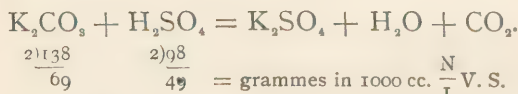
The boiling can then be done at a little distance

from the burette and the expansion of the standard solution therein thus prevented.

Another and better method is to use methyl orange as an indicator, and conduct the process by simple titration without the use of heat.

Methyl orange is not affected by  $\text{CO}_2$ . When methyl orange is used as an indicator, standard sulphuric acid, and not oxalic acid, should be employed. The reaction of the latter with this indicator is not very sharp.

**Potassium Carbonate**,  $\text{K}_2\text{CO}_3 = \left\{ \begin{array}{l} 137.91 \\ *138 \end{array} \right.$ .—Weigh carefully one gramme of the salt, dissolve in a small quantity of water in a beaker or flask, add a few drops of methyl orange T. S., and titrate with normal sulphuric acid until a faint orange-red color appears.



Each cc. of  $\frac{\text{N}}{\text{I}} \text{H}_2\text{SO}_4$ , therefore, represents 0.069 gramme (more accurately 0.068955 gramme) of pure dry potassium carbonate.

Thus if 14.4 cc. of the normal acid were required, the salt contained  $14.4 \times .069 = .9936$  grammes of pure  $\text{K}_2\text{CO}_3$ , or 99.36 per cent. The U. S. P. requirement is that 0.69 grammes of the salt be neutralized by not less than 9.5 cc. of normal acid, corresponding to 95% of the pure salt.\*

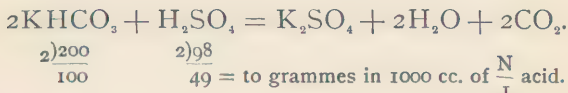
When methyl orange is used the end reaction is not very well defined, and practice is required to obtain good results. If it is desired to use litmus or phenol-

phthalein, it will be necessary to boil the solution as described above.

$$\begin{aligned} & * .069 \times 9.5 = 0.6555 \\ & \frac{0.6555 \times 100}{0.69} = 95\% \end{aligned}$$

**Potassium Bicarbonate**,  $\text{KHCO}_3 = \left\{ \begin{array}{l} 99.88 \\ *_{100} \end{array} \right.$ —

The process is exactly the same as that for the carbonate.

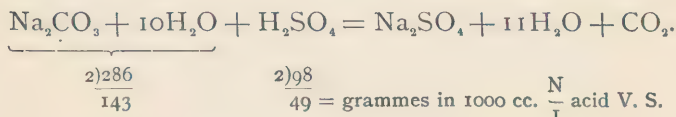


Each cc. of  $\frac{\text{N}}{\text{I}}$  acid represents 0.1 gramme (more exactly 0.09988 gramme) of pure  $\text{KHCO}_3$ .

The U. S. P. requirement is that 1 gramme of the salt be neutralized by not less than 10 cc. of normal acid (corresponding to 100 per cent of the pure salt).

**Sodium Carbonate**,  $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O} = \left\{ \begin{array}{l} 285.45 \\ *_{286} \end{array} \right.$ —

Dissolve two grammes of sodium carbonate in sufficient water, add a few drops of methyl orange, and titrate as described under potassium carbonate.

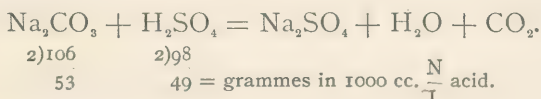


Each cc. of  $\frac{\text{N}}{\text{I}}$  acid V. S. represents 0.143 gramme of crystallized sodium carbonate,



The U. S. P. directs that the salt be deprived of its water of crystallization by heat immediately before being weighed, and that 1 gramme of the anhydrous carbonate should neutralize not less than 18.7 cc. of  $\frac{N}{1}$  sulphuric acid, corresponding to 98.9%.

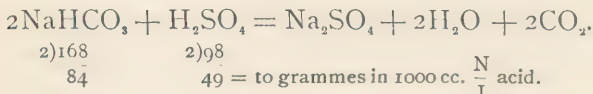
**Sodium Carbonate** (exsiccated).—Operate upon 1 gramme of the salt as described.



Each cc. of the  $\frac{N}{1}$  acid represents .053 gramme of anhydrous sodium carbonate. The U. S. P. requirement is that not less than 13.8 cc. of normal sulphuric acid should neutralize 1 gramme of the salt, corresponding to about 73 per cent of anhydrous sodium carbonate.

$$.053 \times 13.8 = .7314 \quad \text{or} \quad 73.14\%$$

**Sodium Bicarbonate**,  $\text{NaHCO}_3 = \left\{ \begin{array}{l} 83.85 \\ *84 \end{array} \right.$ .—Operate upon 1 gramme of the salt, and proceed in the usual way.



Thus each cc. of  $\frac{N}{1}$  acid represents .084 gramme of pure sodium carbonate.

According to the U. S. P., 0.85 gramme of sodium

bicarbonate should require not less than 10 cc. of normal sulphuric acid, which corresponds to at least 98.6% of the pure salt.

$$.084 \times 10 = .84$$

$$\frac{.84 \times 100}{.85} = 98.6\%$$

$$\text{Lithium Carbonate, Li}_2\text{CO}_3 = \left\{ \begin{array}{l} 73.87 \\ *74 \end{array} \right. .—$$



$$\begin{array}{r} 2)74 \\ 37 \end{array}$$

$$2)98$$

$$49 = \text{grammes in } 1000 \text{ cc. } \frac{\text{N}}{\text{I}} \text{ acid.}$$

Each cc. of  $\frac{\text{N}}{\text{I}}$  acid represents 0.037 gramme of lithium carbonate (more accurately .03693). 0.5 gm. of dry lithium carbonate are mixed with about 20 cc. of water in a beaker, a few drops of methyl orange T. S. added, and titration proceeded with until a faint orange-red color of the solution indicates the complete neutralization of the lithium carbonate.

To comply with the U. S. P. test, 0.5 gm. should require for complete neutralization not less than 13.4 cc. of normal sulphuric acid, corresponding to at least 98.98 per cent of the pure salt.

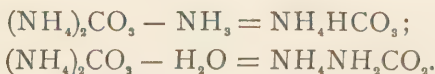
$$0.03693 \times 13.4 = 0.494862 \text{ gm.}$$

$$\frac{0.494862 \times 100}{0.5} = 98.98\%$$

$$\text{Ammonium Carbonate, N}_3\text{H}_{11}\text{C}_2\text{O}_6 = \left\{ \begin{array}{l} 156.77 \\ *157 \end{array} \right. .$$

— Normal ammonium carbonate has the formula

$(\text{NH}_4)_2\text{CO}_3$ , but the normal salt loses upon exposure  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . The commercial salt, therefore, generally is a mixture of carbonate and bicarbonate.

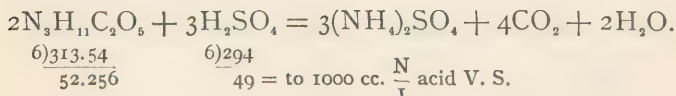


The commercial carbonate is therefore generally expressed thus:



For estimating the carbonate of ammonia the U. S. P. recommends the following procedure: Dissolve 7.84 gms. of unaltered carbonate of ammonia in water to the volume of 90 cc. Take 30 cc. of this solution (which contains 2.613 gms. of the salt), add a few drops of rosolic acid T. S., and titrate with  $\frac{\text{N}}{\text{I}}$   $\text{H}_2\text{SO}_4$  V. S. until the violet-red color is replaced by

yellow. 50 cc. of the  $\frac{\text{N}}{\text{I}}$   $\text{H}_2\text{SO}_4$  should be required before this change takes place, corresponding to 100% of pure salt.



Each cc., therefore, represents 0.052256 gm. of ammonium carbonate.

$$50 \text{ cc.} = 50 \times .052256 = 2.6128 \text{ gms.}$$

$$\frac{2.6128 \times 100}{2.613} = 100\%$$

Although rosolic acid, on account of its sensitiveness to ammonia, is recommended in the U. S. P. process, yet it must be remembered that this indicator is affected by  $\text{CO}_2$ , and therefore great care should be exercised in this estimation. It must also be remembered that if heat is employed to dispel the  $\text{CO}_2$  it is apt to occasion a loss of ammonia.

Methyl orange is not affected by  $\text{CO}_2$  and might be employed in this case, but it is not as sensitive to ammonia as rosolic acid.

The method usually employed by skilled analysts is to add a measured excess of the standard acid solution, and thus convert the ammonium carbonate into the less volatile ammonium sulphate; then gently boil to get rid of  $\text{CO}_2$ , and titrate back with a standard alkaline V. S. (using litmus as an indicator) until the excess of acid is neutralized. The quantity of free acid is thus found, which, when deducted from the amount of acid first added, gives the quantity which was required to neutralize the ammonium carbonate.

Thus, 2.613 gm. in solution of ammonium carbonate are treated with 70 cc. of  $\frac{N}{I} \text{H}_2\text{SO}_4$  V. S., which is more than sufficient to neutralize it; the solution is then gently boiled to drive off  $\text{CO}_2$ , a few drops of litmus tincture added, and then titrated with  $\frac{N}{I} \text{KOH}$  V. S. until the litmus no longer shows an acid reaction and the solution is neutral.

Let us assume that 20 cc. of the  $\frac{N}{I} \text{KOH}$  V. S. were used. By deducting the 20 cc. from the 70 cc. of  $\frac{N}{I}$

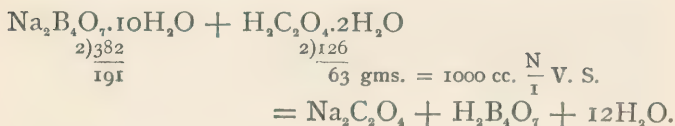
acid first added we find that 50 cc. of the acid went into combination with the ammonium salt. Thus,

$$50 \times .052256 = 2.6128 (*2.613)$$

$$\frac{2.613 \times 100}{2.613} = 100\%$$

**Borax**,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} = \left\{ \begin{smallmatrix} 380.92 \\ *382 \end{smallmatrix} \right.$ .—Two gms. of borax are dissolved in a small quantity of water, a few drops of tincture of litmus are added, and the solution titrated with normal oxalic acid V. S., or some other  $\frac{\text{N}}{\text{I}}$  acid V. S.

Boric acid is liberated during the operation, which colors the litmus wine-red. This is not regarded, and the titration is continued until the bright red, due to the action of free oxalic acid, makes its appearance. Apply the following equation:

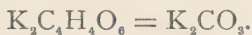


Thus each cc. of  $\frac{\text{N}}{\text{I}}$  oxalic acid V. S. represents 0.191 gm. crystallized borax.

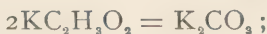
#### ORGANIC SALTS OF THE ALKALIES.

The tartrates, citrates, and acetates of the alkali metals are converted by ignition into carbonates, the whole of the base remaining in the form of carbonate.

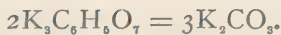
Each molecular weight of a normal tartrate gives when ignited one molecular weight of carbonate:



Every two molecular weights of an acetate or an acid tartrate give one molecular weight of carbonate:



Every two molecular weights of a normal citrate give three molecular weights of carbonate:



These reactions are taken advantage of in volumetric analysis, and the tartrates, citrates, and acetates of the alkalies are indirectly estimated by calculating upon the quantity of carbonate formed by burning them, the quantity of carbonate being found by titration in the usual manner.

**Potassium Tartrate**,  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O} = \left\{ \begin{smallmatrix} 243.66 \\ *244 \end{smallmatrix} \right.$ .—

Two gms. of the salt are placed in a platinum or porcelain crucible and heated to redness in contact with the air until completely charred; that is to say, until nothing is left in the crucible but carbonate and free carbon.

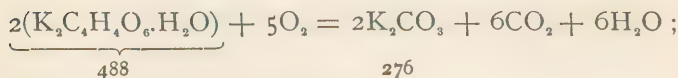
The crucible is now cooled, and its contents treated with boiling water, which dissolves the potassium carbonate, the carbon being separated by filtration. In order to obtain every trace of carbonate it is well to wash the crucible with several small portions of hot

water, and add the washings to the rest of the filtrate through the filter.

If the salt is completely carbonized the filtrate will be colorless, but if the carbonization is not complete the solution will be more or less colored, and should be rejected, and a fresh quantity of the salt subjected to ignition.

To the filtrate, which contains potassium carbonate, add a few drops of methyl-orange, and titrate with  $\frac{N}{I}$  sulphuric acid V. S. until a light orange-red color appears and the carbonate is neutralized.

The following equations will explain the reactions:



then



therefore

$$\underbrace{2(K_2C_4H_4O_6 \cdot H_2O)}_{4)488} = 2K_2CO_3 = 2H_2SO_4, \\ 122 \text{ gms.} = \quad \quad \quad 4)276 \quad \quad \quad 4)196 \\ 69 \text{ gms.} = \quad \quad \quad 49 \text{ gms.} = 1000 \text{ cc. } \frac{N}{I} \text{ V. S.,}$$

and each cc. of  $\frac{N}{I}$   $H_2SO_4$  represents 0.122 gm. of potassium tartrate.

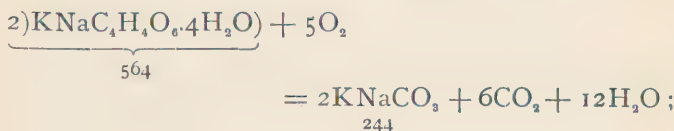
*Example.*—Two gms. of potassium tartrate treated as described above require 16.3 cc. of  $\frac{N}{I}$   $H_2SO_4$  V. S. It therefore contains  $0.122 \times 16.3 = 1.9886$  gms.

$$\frac{1.9886 \times 100}{2} = 99.43\%$$



**Potassium and Sodium Tartrate** (Rochelle Salt),  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O} = \left\{ \begin{smallmatrix} 281.51 \\ *282 \end{smallmatrix} \right.$ .—This salt is treated in exactly the same way as described for potassium tartrate.

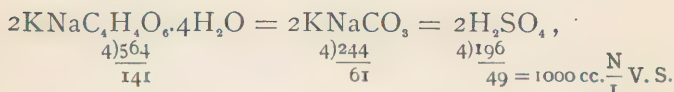
When ignited the double tartrate is converted into a double carbonate of potassium and sodium :



then



therefore



and each cc. of  $\frac{\text{N}}{\text{I}} \text{H}_2\text{SO}_4$  represents 0.141 gm. of  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ .

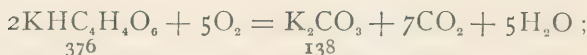
The U. S. P. directs that 1.41 gms. of Rochelle salt when completely decomposed by ignition should leave an alkaline residue, which requires not less than 10cc. of  $\frac{\text{N}}{\text{I}} \text{H}_2\text{SO}_4$  for complete neutralization, corresponding to 100% of the pure salt.

The factor is 0.141 ; 10 cc. = .141  $\times$  10 = 1.41.

$$\frac{1.41 \times 100}{1.41} = 100\%$$

**Potassium Bitartrate** (Cream of Tartar),  $\text{KHC}_4\text{H}_4\text{O}_6$   
 $= \left\{ \begin{array}{l} 187.67 \\ *188 \end{array} \right.$ .—The estimation of this salt is affected in the same way as the tartrate.

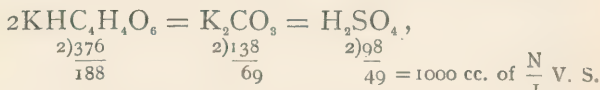
The bitartrate having but one atom of potassium in its molecule, it takes two molecules to form one molecule of carbonate.



then



therefore



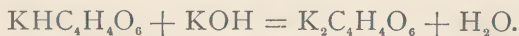
and each cc. of  $\frac{\text{N}}{\text{I}} \text{ H}_2\text{SO}_4 \text{ V. S.} = 0.188 \text{ gm. of } \text{KHC}_4\text{H}_4\text{O}_6$ .

Another way of estimating bitartrate is to dissolve a weighed quantity in hot water and titrate with  $\frac{\text{N}}{\text{I}}$  potassium hydrate until neutral, and thus the amount of tartaric acid existing as bitartrate is found. The bitartrate is always acid in reaction. This latter is the U. S. P. method. In detail it is as follows:

1.88 gms. of the bitartrate are dissolved in 100 cc. of hot water, a few drops of phenolphthalein T. S. added, and then titrated with  $\frac{\text{N}}{\text{I}} \text{ KOH V. S.}$  until a faint pink color indicates that all of the acid has been neutralized.

Not less than 9.9 cc. of the normal alkali should be required, corresponding to 99% of pure salt.

The following equation will show the reaction :



$$188 \qquad 56 = 1000 \text{ cc. of } \frac{\text{N}}{\text{I}} \text{ KOH V. S.}$$

Each cc. of  $\frac{\text{N}}{\text{I}}$  KOH V. S. represents .188 gm. of  $\text{KH C}_4\text{H}_4\text{O}_6$ .

If 9.9 cc. are required for neutralization, then  $9.9 \times .188 = 1.8612$  gms.

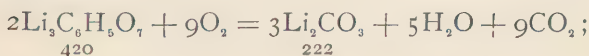
$$\frac{1.8612 \times 100}{1.88} = 99\%$$

**Lithium Citrate,**  $\text{Li}_3\text{C}_6\text{H}_5\text{O}_7 = \left\{ \begin{array}{l} 209.57. \\ *_{210} \end{array} \right.$ —This

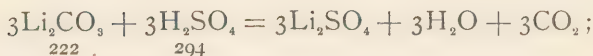
salt is estimated in the same way as the other organic salts.

1 gm. of the salt is thoroughly ignited in a porcelain crucible, and the resulting lithium carbonate mixed with 20 cc. of water and titrated with  $\frac{\text{N}}{\text{I}} \text{ H}_2\text{SO}_4$  V. S. after having added a few drops of methyl-orange T. S. Each cc. of the  $\frac{\text{N}}{\text{I}}$  V. S. used before neutralization is effected represents .070 gm. of pure lithium citrate. The U. S. P. salt requires not less than 14.2 cc. of the  $\frac{\text{N}}{\text{I}}$  V. S.

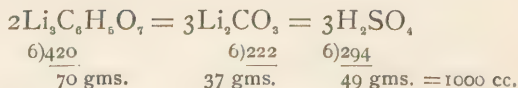
The following are the reactions :



then



therefore



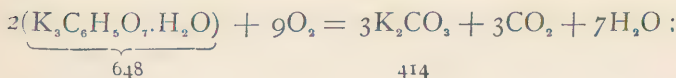
of the  $\frac{\text{N}}{\text{I}}$  sulphuric acid V. S., and thus each cc. of  $\frac{\text{N}}{\text{I}}$   $\text{H}_2\text{SO}_4$  V. S. = .070 gm. of the pure lithium citrate.

If 14.2 cc. of the normal acid are required, then 1 gm. of the salt contains  $.070 \times 14.2 = .994$  gm., or 99.4%. If the more accurate factor .069856 is used, the per cent will be 99.2.

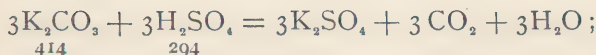
**Potassium Citrate**,  $\text{K}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O} \left\{ \begin{array}{l} 323.59. \\ *324 \end{array} \right.$ —Two

gms. of the salt are placed in a platinum or porcelain crucible and thoroughly ignited at a red heat in contact with air.

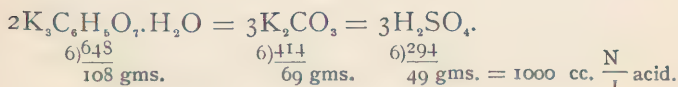
The potassium citrate is thus converted into potassium carbonate, carbon, and gases. When the crucible is cool, hot water is added to its contents, and the solution of potassium carbonate thus obtained is filtered to separate the carbon. To the solution, which must be colorless, add a few drops of methyl-orange T. S., and titrate with  $\frac{\text{N}}{\text{I}}$   $\text{H}_2\text{SO}_4$  V. S. until the change of color indicates complete neutralization. Each cc. of the  $\frac{\text{N}}{\text{I}}$   $\text{H}_2\text{SO}_4$  required before neutralization is effected represents 0.108 gm. of the pure salt.



then



therefore



Thus each cc. of  $\frac{\text{N}}{1}$  acid represents 0.108 gm. of pure potassium citrate.

The U. S. P. directs that 1.080 gms. of potassium citrate be thoroughly ignited at a red heat, and that the alkaline residue should require for complete neutralization not less than 10 cc. of  $\frac{\text{N}}{1}$   $\text{H}_2\text{SO}_4$  V. S. (corresponding to 100% of the pure salt), using methyl-orange as indicator.

The factor, as has been shown, is 0.108 for potassium citrate.

$$.108 \times 10 = 1.08$$

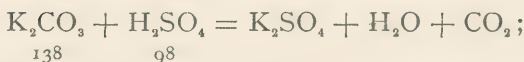
$$\frac{1.08 \times 100}{1.08} = 100\%$$

**Potassium Acetate**,  $\text{KC}_2\text{H}_3\text{O}_2 = \left\{ \begin{array}{l} 97.89 \\ *98 \end{array} \right.$ .—In estimating potassium acetate the salt is ignited and the residue treated in exactly the same manner as in the estimation of the citrates and tartrates before men-

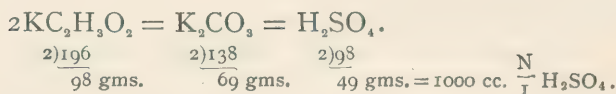
tioned. According to the U. S. P., "if 1 gm. of potassium acetate be by thorough ignition converted into carbonate, the residue should require for complete neutralization not less than 10 cc. of  $\frac{N}{I}$   $H_2SO_4$  V. S. (corresponding to at least 98 per cent of pure potassium acetate), methyl-orange being used as indicator."



then



therefore



Each cc. therefore of  $\frac{N}{I}$   $H_2SO_4$  V. S. corresponds to .098 gm. of potassium acetate.

If 10 cc. are required to neutralize the residue from 1 gm. of potassium acetate, the salt contains  $10 \times .098 = 0.98$  gm., or  $\frac{98}{100}$  of 1 gm., which is 98%.

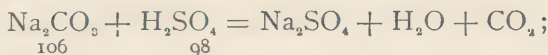
**Sodium Acetate**,  $NaC_2H_3O_2 \cdot 3H_2O = \left\{ \begin{array}{l} 135.74. \\ *136 \end{array} \right.$ —

This salt is estimated in the same manner as the potassium acetate U. S. P. 1.36 gm. of the salt is ignited until completely carbonized, the residue is treated with hot water, the solution thus obtained is filtered, and to the filtrate a few drops of methyl-orange T. S. are added, and then the  $\frac{N}{I}$  sulphuric acid until neutra-

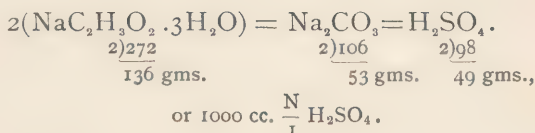
lization is effected. 10 cc. of the latter should be required.



then



therefore



Each cc. therefore represents 0.136 gm. of sodium acetate.

If 10 cc. of the  $\frac{\text{N}}{1}$  acid are required to neutralize, multiply the factor 0.136 gm. by 10 = 1.36 gms.

$$\frac{1.36 \times 100}{1.36} = 100\%$$

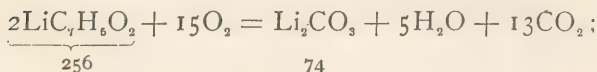
**Lithium Benzoate**,  $\text{LiC}_7\text{H}_5\text{O}_2$   $\left\{ \begin{array}{l} 127.72 \\ *128 \end{array} \right.$ .—This salt when ignited chars, emits inflammable vapors having a benzoin-like odor, and finally leaves a residue of lithium carbonate mixed with free carbon. It may therefore be estimated in the same manner as are the citrates, tartrates, and acetates.

One gm. of the salt is placed in a porcelain crucible and thoroughly ignited. The resulting residue, consisting of lithium carbonate and free carbon, is then mixed with



about 20 cc. of water and a few drops of methyl-orange. The titration is then begun, and each cc. of the  $\frac{N}{I}$   $H_2SO_4$  V. S. used represents about 0.128 gm. of pure lithium benzoate. The U. S. P. requires the salt to be 99.6%.

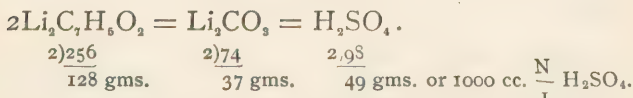
The reactions are expressed as follows:



then



therefore



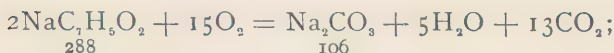
If 7.8 cc. of  $\frac{N}{I}$   $H_2SO_4$  V. S. are used to neutralize the residue from the ignition of the lithium benzoate, then

$$.128 \times 7.8 = .9984 \text{ gm.}; \text{ then } \frac{.9984 \times 100}{I} = 99.84\%$$

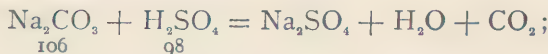
**Sodium Benzoate**,  $NaC_7H_5O_2 = \left\{ \begin{array}{l} 143.71 \\ *144 \end{array} \right.$ .—Ignite 2 gms. of the salt in a porcelain crucible until completely carbonized. Dissolve the residue in about 20 cc. of hot water, filter the solution, rinse the crucible with a little water, and add it through the filter to the

first filtrate. Then add a few drops of methyl-orange T. S. and titrate with  $\frac{N}{I}$   $H_2SO_4$  until neutralization is effected, as shown by the indicator. It should require not less than 13.9 cc. of the  $\frac{N}{I}$   $H_2SO_4$  V. S., which corresponds to 99.8% of pure salt.

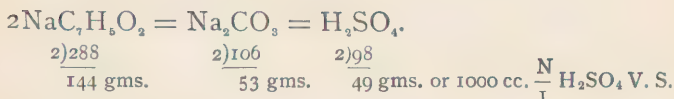
The following are the reactions:



then



therefore



Each cc. of  $\frac{N}{I}$   $H_2SO_4$  V. S. therefore represents 0.144 gm. of sodium benzoate, or more accurately 0.14371.

If 13.9 cc. are required, then the 2 gms. contain  $0.14371 \times 13.9 = 1.997569$ .

$$\frac{1.997569 \times 100}{2} = 99.8\%, \text{ about.}$$

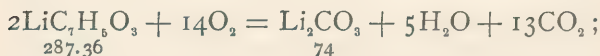
The salicylates of the alkalies are estimated in the same way as are the benzoates, tartrates, etc.

**Lithium Salicylate**,  $\text{LiC}_7\text{H}_5\text{O}_3 = \left\{ \begin{smallmatrix} 143.68 \\ *144 \end{smallmatrix} \right.$ .—Lithium salicylate when heated is decomposed, an odor of phenol is emitted, and a residue of lithium carbonate and carbon is left. It may therefore be estimated as are benzoates, tartrates, citrates, etc.

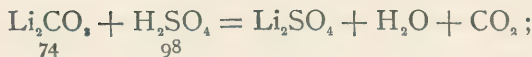
The process is as follows:

Two gms. of the salt are ignited in a porcelain crucible, so as to convert it into carbonate. This carbonate is mixed with about 20 cc. of hot water, a few drops of methyl-orange T. S. added, and then titrated with  $\frac{\text{N}}{\text{I}}$   $\text{H}_2\text{SO}_4$  until neutralized. Not less than 13.8 cc. should be required, each cc. representing 0.14368 gm. of the pure salt.

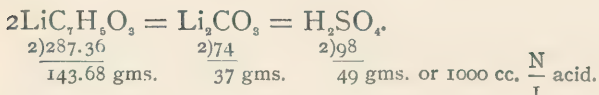
The reactions are:



then



therefore



Each cc. of  $\frac{\text{N}}{\text{I}}$   $\text{H}_2\text{SO}_4$  therefore represents 0.14368 gm. of lithium salicylate.

If 13.8 cc. of  $\frac{N}{1}$   $H_2SO_4$  are required for neutralization, then  $.14368 \times 13.8 = 1.982784$ .

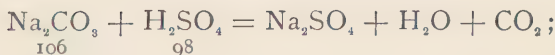
$$\frac{1.982 \times 100}{2} = 99.13\%.$$

**Sodium Salicylate**,  $NaC_7H_5O_3 = \left\{ \begin{smallmatrix} 159.67 \\ *160 \end{smallmatrix} \right.$ .—This salt, when heated, is decomposed, inflammable vapors and an odor of phenol being given off, and a residue of sodium carbonate and free carbon being left.

No volumetric process is given in the U. S. P. for the estimation of this salt. The foregoing processes, however, may be applied to it, the alkaline carbonate which is left being titrated with sulphuric and V. S., each cc. of  $\frac{N}{1}$   $H_2SO_4$  V. S. representing 0.15967 gm., or approximately 0.160 gm., of the pure salicylate.



then



therefore

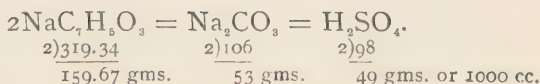


TABLE SHOWING THE APPROXIMATE NORMAL FACTORS, ETC., OF THE ORGANIC SALTS OF THE ALKALINE METALS.

Substance.	Formula.	Molecular Weight.	Equivalent Weight in Carbonate.	Normal Factor.*
Lithium benzoate.....	$\text{LiC}_7\text{H}_5\text{O}_2$	128	37	0.128
“ citrate. ....	$\text{Li}_3\text{C}_6\text{H}_5\text{O}_7$	210	111	0.070
“ salicylate.....	$\text{LiC}_7\text{H}_5\text{O}_3$	144	37	0.144
Sodium acetate.....	$\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$	136	53	0.136
“ benzoate. ....	$\text{NaC}_7\text{H}_5\text{O}_2$	144	53	0.144
“ salicylate.....	$\text{NaC}_7\text{H}_5\text{O}_3$	160	53	0.160
Potassium acetate.....	$\text{KC}_2\text{H}_3\text{O}_2$	98	69	0.098
“ bitartrate. ....	$\text{KHC}_4\text{H}_4\text{O}_6$	188	69	0.188
“ citrate.....	$\text{K}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$	324	207	0.108
“ tartrate.....	$\text{K}_2\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$	244	138	0.122
“ and sodium tartrate.....	$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	282	122	0.141

\* This is the coefficient by which the number of cc. of normal solution used is to be multiplied in order to obtain the quantity of pure substance present in the material examined.

#### ACIDIMETRY.—ESTIMATION OF ACIDS BY NEUTRALIZATION.

In the previous experiments it has been shown how alkalis are estimated by the use of acid solutions of known neutralizing power. In the estimation of acids, which will now be described, the order is reversed, alkaline solutions of known power being used in determining the strength of acids.

Either an alkaline carbonate or an alkaline hydroxide may be used in the form of standard solution for this purpose.

The hydroxide, however, is to be preferred, for the carbonate when used for titrating an acid gives off carbonic-acid gas ( $\text{CO}_2$ ), which interferes to a great extent with the indicators.

In the U. S. P., 1890, volumetric solutions of both potassium and sodium hydroxides are official. The former, however, is preferable, because it attacks glass more slowly and less energetically, and also foams much less than does the sodium hydroxide. The neutralizing power of each is, however, the same.

The caustic alkalies and their solutions are very prone to absorb carbon dioxide from the atmosphere. Therefore the solutions often contain some carbonates, the presence of which will occasion errors when used with most indicators, especially litmus and phenolphthalein. Hence when these indicators or others which are affected by carbon dioxide are used gentle heat should be employed toward the close of each titration to drive off the liberated gas.

The standard solutions of alkaline hydroxides should always be preserved in small vials provided with well-fitting cork or rubber stoppers.

In order to keep solutions of this kind special vessels have been devised (see Fig. 22). The bottle is provided with a well-fitting rubber stopper through which a tube passes, which is filled with a mixture of soda and lime, which absorbs  $\text{CO}_2$  and prevents its access to the solution.

An improvement upon this is shown in Fig. 23, since it allows of the burette being filled without removing the stopper, and consequently without any access of  $\text{CO}_2$  whatever.

**Preparation of Normal Potassium Hydroxide Volumetric Solution,**  $\text{KOH} = \left\{ \begin{array}{l} 55.99 \\ *_{56} \end{array} \right\}$  contains  $\left\{ \begin{array}{l} 55.99 \\ *_{56} \end{array} \right\}$  gms. in 1 litre.—Potassium hydroxide is so prone to absorb carbon dioxide that the pure substance is not

readily obtained in commerce. If pure potassa were easily obtained it would only be necessary to dissolve 56 gms. in sufficient water to make a litre. But since it always contains some  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , it is necessary



FIG. 22.

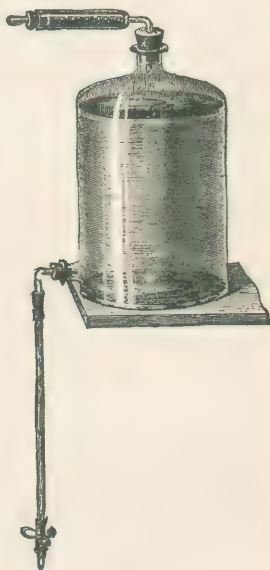


FIG. 23.

to take a slight excess and dilute the solution to the proper volume after having determined its strength.

The U. S. P. process is as follows: Dissolve 75 gms. of potassa in sufficient water to make about 1050 cc. at  $15^\circ \text{C}$ . ( $59^\circ \text{F}$ .), and fill a burette with a portion of this solution.

Dissolve 0.63 gm. of pure oxalic acid in about 10 cc. of water in a beaker or flask, add a few drops of phenolphthalein T. S., and then carefully add from the



burette the potassium-hydroxide solution, agitating frequently and regulating the flow to drops towards the end of the operation until a permanent pale-pink color is obtained. Note the number of cc. of the potassa solution consumed, and then dilute the remainder so that exactly 10 cc. of the diluted liquid will be required to neutralize 0.63 gm. of oxalic acid. Instead of weighing off 0.63 gm. of the acid, 10 cc. of its normal solution may be used.

*Example.*—Assuming that 8 cc. of the stronger potassa solution had been consumed in the trial, then each 8 cc. must be diluted to 10 cc., or the whole of the remaining solution in the same proportion. Thus if 8 cc. must be diluted to 10 cc., 1000 cc. must be diluted to 1250 cc.

$$8 : 10 :: 1000 : x \quad x = 1250 \text{ cc.}$$

It is always advisable to make another trial after diluting. 10 cc. should then neutralize 0.63 gm. of pure oxalic acid.

#### **Centinormal Potassium Hydroxide V. S., KOH**

$= \left\{ \begin{array}{l} 55.99 \\ *_{56} \end{array} \right\}$  contains  $\left\{ \begin{array}{l} 0.5599 \text{ gm.} \\ 0.56 \text{ gm.} \end{array} \right\}$  in 1 litre.—This is made by diluting 10 cc. of the normal solution with enough distilled water to make 1000 cc.

#### **Normal Sodium Hydroxide V. S., NaOH =**

$\left\{ \begin{array}{l} 39.96 \\ *_{40} \end{array} \right\}$  contains  $\left\{ \begin{array}{l} 39.96 \text{ gms.} \\ 40 \text{ gms.} \end{array} \right\}$  in 1 litre.—Dissolve 54 gms. of sodium hydroxide in enough water to make about 1050 cc. at 15° C. (59° F.), and fill a burette with a portion of this solution.

Dissolve 0.63 gm. of pure oxalic acid in about 10 cc. of water in a flask or beaker, add a few drops of phenolphthalein T. S., and then carefully add from a burette

the soda solution, agitating the flask or beaker frequently, as directed under  $\frac{N}{1}$  KOH V. S., until a permanent pale-pink color is produced. Note the number of cc. of soda solution consumed, and then dilute the remainder of the solution so that exactly 10 cc. will be required to neutralize 0.63 gm. of pure oxalic acid.

*Example.* — If 8 cc. of the stronger soda solution had been consumed in the trial, then each 8 cc. must be diluted to 10 cc., or the whole of the remaining solution in the same proportion. Thus if 980 cc. should be still remaining, this must be diluted with water to make  $1233\frac{1}{3}$  cc.

Now make a new trial with the diluted solution to see whether 10 cc. will be required to neutralize 0.63 gm. of oxalic acid (or 10 cc. of  $\frac{N}{1}$  oxalic acid V. S.).

The neutralizing power of this solution is exactly the same as that of  $\frac{N}{1}$  potassium hydroxide V. S., and may be employed in place of the latter, volume for volume.

The following acids may be tested with either or these alkaline solutions :

Acidum aceticum.

“ “ dilutum.

“ “ glaciale.

“ citricum.

“ hydrobromicum dilutum.

“ hydrochloricum.

“ “ dilutum.

“ hypophosphorosum dilutum.

“ lacticum.

Acidum nitricum.

“ “ dilutum.

“ phosphoricum.

“ “ dilutum.

“ sulphuricum.

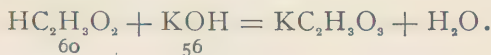
“ “ aromaticum.

“ “ dilutum.

“ tartaricum.

**Acidum Aceticum**,  $\text{HC}_2\text{H}_3\text{O}_2 = \left\{ \begin{array}{l} 59.86 \\ *60 \end{array} \right.$ . — The U. S. P. acetic acid contains 36%, by weight, of absolute  $\text{HC}_2\text{H}_3\text{O}_2$  and 64% of water.

Mix 3 gms. of the acid with a small quantity of water, add a few drops of phenolphthalein T. S., and titrate with normal potassium hydroxide V. S. until a permanent pale-pink color is obtained, and apply the following equation:



Thus 56 gms. or 1000 cc. of  $\frac{\text{N}}{\text{I}}$  KOH V. S. will neutralize 60 gms. of acetic acid; therefore each cc. of  $\frac{\text{N}}{\text{I}}$  KOH V. S. represents .060 gm. of acetic acid.

If 18 cc. are required to neutralize 3 gms. of the acid, it contains  $18 \times .060 = 1.08$  gms. of absolute acetic acid.

$$\frac{1.08 \times 100}{3} = 36\%.$$

According to the U. S. P., 6 gms. of the acid should require 36 cc. of  $\frac{\text{N}}{\text{I}}$  KOH V. S. for complete neutralization.

**Acidum Aceticum Dilutum.**—A solution containing 6%, by weight, of absolute acetic acid.

The estimation is conducted exactly as the above. The diluted acetic acid U. S. P. should contain 6% of absolute acid. 24 gms. should require 24 cc. of  $\frac{N}{I}$  KOH V. S.

$$\begin{aligned} 24 \times .060 &= 1.440 \\ \frac{1.440 \times 100}{24} &= 6\% \end{aligned}$$

**Vinegar.**—Vinegar is impure diluted acetic acid. Its strength may be estimated in the same manner as acetic acid. Phenolphthalein must be used as an indicator. Litmus will give only approximate results, because potassium and sodium acetate both have a slightly alkaline reaction with litmus, but show no reaction with phenolphthalein.\* The absence of mineral acids must be assured before the volumetric test is applied.

The strength of vinegar may also be estimated by distilling 110 cc. until 100 cc. come over. The 100 cc. will contain 80% of the whole acetic acid present in the 110 cc., and may be titrated; or the specific gravity of the distillate may be taken, and, by consulting the table below, the per cent strength of the distillate found. By adding 20% to this the strength of the original vinegar is obtained.

Vinegar usually contains from 3% to 6% of acetic acid.

\* Even dark-colored vinegar may be titrated in this way when diluted. If the color, however, is too dark, litmus-paper or phenolphthalein paper may be used by bringing a drop of the liquid in contact with the paper from time to time during the titration.

ACETIC ACID TABLE.

Per cent of Absolute Acetic Acid.	Specific Gravity at $\left\{ \begin{array}{l} 15^{\circ} \text{ C.} \\ 59^{\circ} \text{ F.} \end{array} \right.$	Per cent of Absolute Acetic Acid.	Specific Gravity at $\left\{ \begin{array}{l} 15^{\circ} \text{ C.} \\ 59^{\circ} \text{ F.} \end{array} \right.$	Per cent of Absolute Acetic Acid.	Specific Gravity at $\left\{ \begin{array}{l} 15^{\circ} \text{ C.} \\ 59^{\circ} \text{ F.} \end{array} \right.$
1	1.0007	26	1.0363	51	1.0623
2	1.0022	27	1.0375	52	1.0631
3	1.0037	28	1.0388	53	1.0638
4	1.0052	29	1.0400	54	1.0646
5	1.0067	30	1.0412	55	1.0653
6	1.0083	31	1.0424	56	1.0660
7	1.0098	32	1.0436	57	1.0666
8	1.0113	33	1.0447	58	1.0673
9	1.0127	34	1.0459	59	1.0679
10	1.0142	35	1.0470	60	1.0685
11	1.0157	36	1.0481	61	1.0691
12	1.0171	37	1.0492	62	1.0697
13	1.0185	38	1.0502	63	1.0702
14	1.0200	39	1.0513	64	1.0707
15	1.0214	40	1.0523	65	1.0712
16	1.0228	41	1.0533	66	1.0717
17	1.0242	42	1.0543	67	1.0721
18	1.0256	43	1.0552	68	1.0725
19	1.0270	44	1.0562	69	1.0729
20	1.0284	45	1.0571	70	1.0733
21	1.0298	46	1.0580	71	1.0737
22	1.0311	47	1.0589	72	1.0740
23	1.0324	48	1.0598	73	1.0742
24	1.0337	49	1.0607	74	1.0744
25	1.0350	50	1.0615	75	1.0746

## ESTIMATION OF FREE MINERAL ACIDS IN VINEGAR.

Mr. Hehner has devised the method given below, which has the merit of being speedy, scientific, and accurate.

The method is based upon the fact that acetates of the alkalies are always present in commercial vinegar, and when vinegar is evaporated to dryness, and the ash ignited, the acetates of the alkalies are thus converted into carbonates. If the ash has an alkaline reaction no free mineral acid is present. If, however, the ash is

neutral or acid some free mineral acid must be present.

The quantitative process in detail is as follows: 50 cc. of vinegar are mixed with 25 cc. of  $\frac{N}{1}$  soda or potash V. S. The liquid is evaporated to dryness on a water-bath, and the residue carefully incinerated at the lowest possible temperature, to convert the acetates into carbonates. When cooled, 25 cc. of  $\frac{N}{10}$  sulphuric acid V. S. are added, the mixture heated to expel  $\text{CO}_2$  and filtered. The filter is washed with hot water, phenolphthalein T. S. added, and the filtrate and washings carefully titrated with  $\frac{N}{10}$  alkali. Each cc. of  $\frac{N}{10}$  alkali used represents 0.0049 gm.  $\text{H}_2\text{SO}_4$  or 0.003637 gm.  $\text{HCl}$ .

**Acidum Aceticum Glaciale.**—Three gms. of glacial acetic acid are mixed with a small quantity of water, a few drops of phenolphthalein T. S. added, and the solution titrated with  $\frac{N}{1}$  potassium hydroxide V. S. until a very pale pink color appears. Each cc. represents .06 gm. of absolute acetic acid.

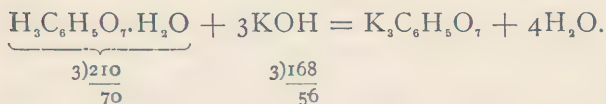
49.5 cc. are required by 3 gms. of the U. S. P. acid.

$$\begin{aligned} 49.5 \times .06 &= 2.970 \text{ gms.} \\ \frac{2.970 \times 100}{3} &= 99\% \end{aligned}$$

**Acidum Citricum,**  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O} = \left\{ \begin{array}{l} 209.5 \\ *_{210} \end{array} \right.$ .—  
3.5 gms. of citric acid are dissolved in a sufficient quantity of water, a few drops of phenolphthalein added, and the solution titrated with  $\frac{N}{1}$  potassium hydroxide

V. S. until a very pale pink color appears. Each cc. of  $\frac{N}{1}$  potassium hydroxide consumed before neutralization is effected represents .070 gm. of the pure acid, and 50 cc. should be required.

The reaction is expressed by the following equation:



Thus 56 gms. of KOH or 1000 cc. of its normal solution represent 70 gms. of pure crystallized acid, and each cc. represents .070 gm. Therefore

$$50 \times .070 = 3.5 \text{ gms.}$$

$$\frac{3.5 \times 100}{3.5} = 100\%$$

**Lime-juice or Lemon-juice**, the chief constituent of which is citric acid, may be estimated by titrating with  $\frac{N}{1}$  potassium hydroxide V. S. in the same manner as other acid solutions.

Lime-juice contains on an average 7.84%, rarely as much as 10%, and very seldom as little as 7% of citric acid.

Commercial lime-juice frequently contains sulphuric, hydrochloric, or tartaric acid. Therefore before applying this test the absence of notable quantities of these acids must be insured by qualitative tests.

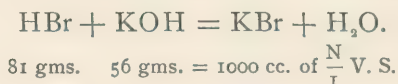
**Acidum Hydrobromicum Dilutum** (Diluted Hydrobromic Acid),  $\text{HBr} = \left\{ \begin{array}{l} 80.76 \\ *81 \end{array} \right.$ .—A liquid containing 10



per cent. of pure hydrobromic acid (HBr) and 90 per cent. of water.

8.1 gms. of the acid are diluted with a small quantity of water, a few drops of phenolphthalein T. S. added, and then  $\frac{N}{I}$  potassium hydroxide V. S. added from a burette, until a very faint pink color is produced. Note the quantity of  $\frac{N}{I}$  alkali used, and multiply this by the factor .081 gm. to obtain the weight of HBr in the diluted acid taken.

The reaction is expressed by the following equation:



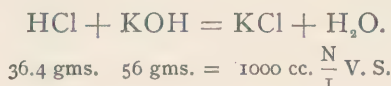
Each cc. therefore represents .081 gm., or 1 per cent, of HBr.

If this acid is made with tartaric acid and potassium bromide, a white, crystalline precipitate will be produced upon the addition of the  $\frac{N}{I}$  alkali, some of which will be neutralized by the dissolved potassium bitartrate and the excess of tartaric acid, and an incorrect indication will be given.

**Acidum Hydrochloricum** (Muriatic Acid),  $\text{HCl} = \left\{ \begin{array}{l} 36.37 \\ *36.4 \end{array} \right.$ . — A liquid containing 31.9 per cent., by weight, of absolute  $\text{HCl}$  and 68.1 per cent. of water.

3 gms. of hydrochloric acid are diluted with a little water, a few drops of phenolphthalein added, and then  $\frac{N}{I}$  potassium hydroxide V. S. from a burette, until a

faint pink color is produced. Note the quantity of  $\frac{N}{I}$  alkali used, and apply the following equation:



Each cc. of  $\frac{N}{I}$  alkali required before the acid is neutralized represents .0364 gm. of pure HCl.

3.64 gms. of the U.S.P. acid should require for complete neutralization 31.9 cc. of  $\frac{N}{I}$  KOH V. S.

Diluted hydrochloric acid, U. S. P., contains 10 per cent. of absolute HCl. 3.64 gms. of the diluted acid should require for neutralization 10 cc. of  $\frac{N}{I}$  KOH V. S.

Let us assume that the 3 gms. of hydrochloric acid required 20 cc. of  $\frac{N}{I}$  KOH V. S. Then

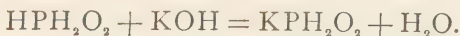
$$20 \times .0364 = .7280 \text{ gm.}$$

of pure HCl in 3 gms. of the acid.

$$\frac{.7280 \times 100}{3} = 24.26\%$$

**Acidum Hypophosphorosum Dilutum** (Diluted Hypophosphorous Acid).—The U. S. P. acid contains 10 per cent. of absolute  $\text{HPH}_2\text{O}_2 = \left\{ \begin{array}{l} 65.88. \\ *66 \end{array} \right.$

This acid is estimated in exactly the same way as the acids previously noticed :



$$66 \text{ gms.} = 56 \text{ gms.} = 1000 \text{ cc. } \frac{\text{N}}{\text{I}} \text{ alkali.}$$

Thus each cc. of  $\frac{\text{N}}{\text{I}}$  alkali represents .066 gm. of  $\text{HPH}_2\text{O}_2$ .

Take 5 gms. of the acid, dilute it with a small quantity of water, add a few drops of phenolphthalein T. S., and titrate with  $\frac{\text{N}}{\text{I}}$  KOH V. S. until a very faint pink color appears. If 8 cc. of the  $\frac{\text{N}}{\text{I}}$  alkali are used, the 5 gms. contain  $8 \times .066 = .528$  gm.

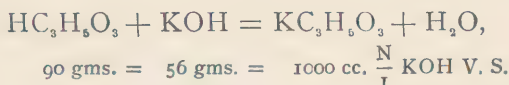
$$5 : .528 :: 100 : x. \quad x = 10.56\%$$

6.6 gms. of the U. S. P. acid should require for neutralization 10 cc. of  $\frac{\text{N}}{\text{I}}$  KOH V. S.

**Acidum Lacticum**,  $\text{HC}_3\text{H}_5\text{O}_3 = \left\{ \begin{array}{l} 89.79 \\ *90 \end{array} \right.$ .—An organic acid containing 75 per cent., by weight, of absolute lactic acid and 25 per cent. of water.

5 gms. of lactic acid are slightly diluted with water, a few drops of phenolphthalein T. S. added, and then the  $\frac{\text{N}}{\text{I}}$  KOH V. S. from a burette, until a pale-pink color is produced. Note the quantity of normal alkali used,

and multiply that number by .090 gm. to get the quantity of absolute acid in the 5 gms. taken.



and 1 cc. of  $\frac{\text{N}}{\text{I}}$  KOH = .090 gm. of  $\text{HC}_3\text{H}_5\text{O}_3$ .

If 40 cc. of  $\frac{\text{N}}{\text{I}}$  KOH are required for neutralization of the 5 gms. of the lactic acid, then

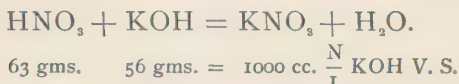
$$\begin{aligned} \times 40 .09 &= 3.60 \text{ gms.} \\ 5 : 3.6 :: 100 : x. \quad x &= 72\% \end{aligned}$$

**Acidum Nitricum** (Nitric Acid),  $\text{HNO}_3 = \left\{ \begin{array}{l} 62.89 \\ *63 \end{array} \right.$

—The U. S. P. acid contains 68 per cent., by weight, of absolute nitric acid and 32 per cent. of water.

Take 3 gms. of nitric acid, dilute with a little water, add a few drops of phenolphthalein T. S., and then pass into the mixture from a burette  $\frac{\text{N}}{\text{I}}$  potassium hydroxide V. S. until neutralization is effected, and the liquid acquires a faint pink color.

Apply the following equation :



Thus each cc. of  $\frac{\text{N}}{\text{I}}$  KOH V. S. required before neutralization is effected represents 0.063 gm. of absolute nitric acid.

If 30 cc. of the  $\frac{N}{I}$  alkali are required, then the 3 gms. contain  $.063 \times 30 = 1.890$  gms.

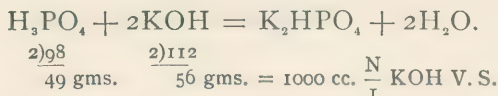
$$3 : 1.89 :: 100 : x. \quad x = 63\%$$

3.145 gms. of the U. S. P. acid require 34 cc. of  $\frac{N}{I}$  KOH V. S., which corresponds to 68% of absolute acid.

*Acidum Nitricum Dilutum*, U. S. P., contains 10% of absolute nitric acid, and is estimated in the same way as the nitric acid.

**Acidum Phosphoricum** (Phosphoric Acid),  $H_3PO_4$ ,  $= \left\{ \begin{array}{l} 97.8 \\ *98 \end{array} \right.$ .—The U. S. P. acid contains 85% of absolute orthophosphoric acid and 15% of water.

Take 1 gm. of phosphoric acid, dilute it with water, add a few drops of phenolphthalein T. S., and titrate with  $\frac{N}{I}$  potassium hydroxide V. S. until neutralization is complete and the liquid has acquired a faint pink color.



Thus each cc. of  $\frac{N}{I}$  KOH required represents .049 gm. of absolute orthophosphoric acid.

If 1 gm. of the acid requires for neutralization 18 cc. of  $\frac{N}{I}$  KOH V. S., it contains

$$.049 \times 18 = .922 \text{ gm. or } 92.2\%$$

0.98 gm. of the U. S. P. acid should require 17 cc. of  $\frac{N}{I}$  KOH V. S., which means 85% of absolute phosphoric acid.

In the estimation of phosphoric acid litmus cannot be used as an indicator, for the disodic or dipotassic hydric phosphate ( $\text{Na}_2\text{HPO}_4$  or  $\text{K}_2\text{HPO}_4$ ) which is formed when the standard alkaline solution is added to free tribasic phosphoric acid is slightly alkaline to litmus, but not to phenolphthalein.

It is recommended, therefore, in order to estimate phosphoric acid alkalimetrically, to prevent the formation of soluble phosphate of the alkali, and to bring the acid into a definite compound with an alkaline earth as follows:

The free acid in a diluted state is placed in a flask and a known volume of normal alkali in excess added in order to convert the whole of the acid into a basic salt. A few drops of rosolic acid are now added, and sufficient neutral  $\text{BaCl}_2$  solution poured in to combine with the phosphoric acid. The mixture is heated to boiling, and while hot the excess of alkali is titrated with  $\frac{N}{I}$  acid.

The suspended basic phosphate, together with the liquid, possesses a rose-red color until the last drop or two of acid, after continuous heating and agitation, gives a permanent white or slightly yellowish milky appearance, when the process is ended.

The volume of normal alkali, less the volume of normal acid, represents the amount of alkali required to convert the phosphoric acid into a normal trisodic or tripotassic phosphate.



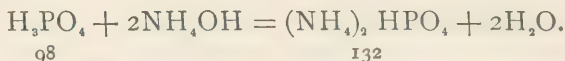
$$\begin{array}{r} 3)98 \\ 32.66 \text{ gms.} \end{array} \quad \begin{array}{r} 3)168 \\ 56 \text{ gms.} \end{array} = 1000 \text{ cc. of } \frac{\text{N}}{\text{I}} \text{ KOH V. S.}$$

Thus 1 cc. of  $\frac{\text{N}}{\text{I}}$  alkali = .03266 gm. of  $\text{H}_3\text{PO}_4$ .

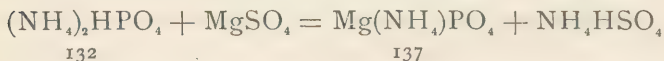
Diluted phosphoric acid is estimated in the same manner.

**Phosphoric Acid** may also be estimated by Stolba's method, as *Ammonia-magnesian Phosphate*.

0.2 gm. of phosphoric acid is supersaturated with ammonia water, so as to convert all of the acid into ammonium phosphate and leave an excess of the alkali.



An excess of magnesia mixture\* is now added in order to precipitate all of the phosphoric acid in the form of ammonia-magnesian phosphate.



The precipitate is washed, first with ammonia water, and then the ammonia is entirely removed by washing with alcohol of 50% or 60% strength.

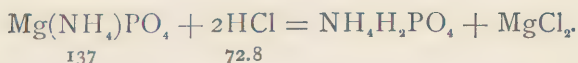
The precipitate is now dissolved in a measured excess of  $\frac{\text{N}}{10}$  hydrochloric acid V. S., a few drops of methyl-orange T. S. added, and the excess of acid

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\* **Magnesia Mixture.**—Dissolve 10 gms. of magnesium sulphate and 20 gms. of ammonium chloride in 80 cc. of water, add 42 cc. of ammonia water, set aside for a few days in a well-stoppered bottle, and filter. It should never be used freshly made.



found by titrating back with  $\frac{N}{10}$  potassium hydrate. The difference between the number of cc. of  $\frac{N}{10}$  HCl added and the quantity of  $\frac{N}{10}$  KOH used gives the quantity of HCl which went into combination with the ammonia-magnesian phosphate.



By consulting the equations given, it will be seen that 72.8 gms. of HCl are equivalent to 137 gms. of  $\text{Mg}(\text{NH}_4)\text{PO}_4$ , or 132 gms. of  $(\text{NH}_4)_2\text{HPO}_4$ , or 98 gms. of  $\text{H}_3\text{PO}_4$ .

This means that 1000 cc. of a decinormal  $\left(\frac{N}{10}\right)$  solution of HCl, containing 3.64 gms. of the acid, represents  $\frac{1}{250}$  of each of these quantities; and one cc. of  $\frac{N}{10}$  HCl thus represents 0.0049 gm. of phosphoric acid.

In this estimation care must be taken that all free ammonia is removed from the precipitate, and that the whole of the ammonia-magnesian phosphate is decomposed by the acid before titration with the  $\frac{N}{10}$  alkali. This may be insured by using a rather large excess of the acid and warming.

*Example.*—To the precipitate of ammonia-magnesian phosphate obtained from 0.2 gm. of phosphoric acid, 50 cc. of  $\frac{N}{10}$  HCl are added. In titrating back 15.3

cc. of  $\frac{N}{10}$  KOH are required. Hence 34.7 cc. of the acid went into combination with the double salt.

Then  $34.7 \times .0049 = 0.17003$  gm.,

and  $\frac{.17003 \times 100}{.2} = 85.01\%$  of absolute phosphoric acid. This method is said to give good results.

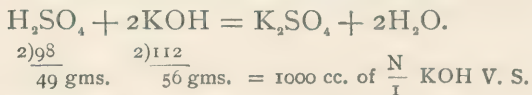
**Acidum Sulphuricum**,  $H_2SO_4 = \left\{ \begin{array}{l} 97.82 \\ *98 \end{array} \right.$ .—U. S. P. sulphuric acid contains 92.5 per cent., by weight, of absolute sulphuric acid and 7.5 per cent. of water.

*Aromatic Sulphuric Acid* U. S. P. contains 18.5% of absolute sulphuric acid, by weight.

*Diluted Sulphuric Acid* U. S. P. contains 10% by weight of absolute sulphuric acid. Operate upon 1 gm. of the strong acid or upon 5 gms. of either dilute or aromatic sulphuric acid.

One gm. of sulphuric acid is diluted with about 10 cc. of water. Add a few drops of phenolphthalein T. S. and titrate with  $\frac{N}{I}$  potassa V. S. until the acid is neutralized and the solution has acquired a faint pink color. Each cc. of  $\frac{N}{I}$  alkali solution represents 0.049 gm. of absolute sulphuric acid.

The reaction is shown by the following equation :



If 18 cc. of  $\frac{N}{I}$  KOH V. S. are required for the complete neutralization of the sulphuric acid, then it contains  $18 \times .049$  gm. = 0.882 gm.

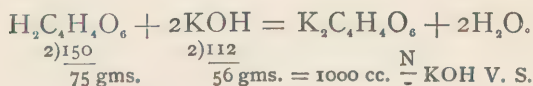
$1 : 0.882 :: 100 : x$   $x = 88.2\%$  absolute sulphuric acid.

**Diluted Sulphuric Acid** is estimated in the same way. Operate upon 5 gms. instead of upon 1 gm.

**Aromatic Sulphuric Acid** contains ethyl sulphuric acid. Therefore in estimating the sulphuric acid in this preparation it must be boiled with water for a few minutes so as to decompose the ethyl sulphuric acid. The mixture is then allowed to cool, and titrated in the usual manner with  $\frac{N}{I}$  KOH V. S., using phenolphthalein as indicator.

The U. S. P. requires that 4.89 gms. when mixed with 15 cc. of water and boiled for several minutes should, after cooling, be neutralized by not less than 18.5 cc. of  $\frac{N}{I}$  KOH.

**Acidum Tartaricum** (Tartaric Acid),  $H_2C_4H_4O_6 =$   
 $\left\{ \begin{array}{l} 149.64 \\ *150 \end{array} \right.$ .—Dissolve 3.75 gms. of tartaric acid in sufficient water to make a solution, add a few drops of phenolphthalein T. S., and then pass into the solution from a burette  $\frac{N}{I}$  potassium hydroxide V. S. until a faint pink tint is acquired by the solution, and apply the equation



Thus each cc. required for the neutralization of the acid represents 0.075 gm. If 50 cc. are required, then  $50 \times .075 = 3.75$  gms. or 100%.

TABLE SHOWING THE APPROXIMATE NORMAL FACTORS, ETC., FOR THE ACIDS.

Acid.	Formula.	Molecular Weight.	Normal Factors.*
Acetic .....	$\text{HC}_2\text{H}_3\text{O}_2$	60	.060
Citric .....	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$	210	.070
Hydrobromic .....	$\text{HBr}$	81	.081
Hydrochloric .....	$\text{HCl}$	36.4	.0364
Hypophosphorous .....	$\text{HPH}_2\text{O}_2$	66	.066
Lactic .....	$\text{HC}_3\text{H}_5\text{O}_3$	90	.090
Nitric .....	$\text{HNO}_3$	63	.063
Phosphoric .....	$\text{H}_3\text{PO}_4$	98	.049
Sulphuric .....	$\text{H}_2\text{SO}_4$	98	.049
Tartaric .....	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	150	.075

Phosphoric, after conversion into a neutral phosphate and retitrating with  $\frac{\text{N}}{\text{I}}$  acid = ..... .03266

Phosphoric acid, as ammonia-magnesian phosphate with decinormal acid = ..... .0049

\* This is the coefficient by which the number of cc. of normal solution used is to be multiplied in order to obtain the quantity of pure acid in the sample analyzed.

#### ESTIMATION OF THE SALTS OF THE ALKALINE EARTHS.

Standard solution of hydrochloric or of nitric acid is preferred by many operators for the titration of caustic or carbonated alkaline earths.

These acids have the advantage over most other acids in forming soluble salts.

The hydroxides may be estimated by any of the indicators, but as they readily absorb  $\text{CO}_2$  out of the air, they are generally contaminated with more or less carbonate, and the residual method should be used, i.e., a known excess of standard acid should be added, the mixture boiled to expel any trace of  $\text{CO}_2$ , and re-titrated with standard alkali.

The carbonates are of course estimated in the same way.

If methyl-orange is used, heat need not be employed, unless it is impossible to dissolve the substance in the cold. A good excess of acid is, however, generally sufficient.

Soluble salts of calcium, barium, and strontium, such as chlorides, nitrates, etc., may be readily estimated as follows :

A weighed quantity of the salt is dissolved in water, cautiously neutralized if it is acid or alkaline, phenolphthalein is added, the mixture heated to boiling, and standard solution of sodium carbonate delivered in from time to time, with boiling until the red color is permanent.

This process depends upon the fact that sodium carbonate forms with soluble salts of these bases insoluble and neutral carbonates.



Magnesium salts cannot be estimated in this way, as magnesium carbonate affects the indicator.

The alkaline earth salts may also be estimated by dissolving them in water, precipitating the base as carbonate, with an excess of ammonium carbonate and some free ammonia.

The mixture is heated for a few minutes, and the carbonate separated by filtration, thoroughly washed with hot water till all soluble matters are removed, and then titrated with normal acid V. S. as carbonate.

**Normal Sodium Carbonate V. S.**— $\text{Na}_2\text{CO}_3 =$   
 $\left\{ \begin{array}{l} 105.85 \\ *106 \end{array} \right\}$  contains  $\left\{ \begin{array}{l} 52.925 \\ *53. \end{array} \right\}$  gms. in 1 litre.—This solution is made by dissolving 53 gms. of pure sodium car-

bonate (anhydrous) previously ignited and cooled, in distilled water, and diluting to 1 litre at 15° C. (59° F.).

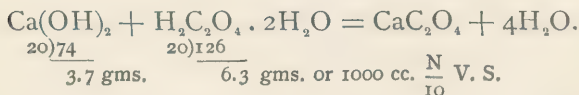
If pure salt is not at hand the solution may be made as follows:

About 85 gms. of pure sodium bicarbonate, free from thiosulphate, chloride, etc., are heated to dull redness (not to fusion) for about fifteen minutes to expel one half of the  $\text{CO}_2$ ; it is then cooled under a desiccator. When cool, weigh off 53 gms. and dissolve it in distilled water to 1 litre at 15° C. (59° F.). This solution should neutralize  $\frac{N}{1}$  acid V. S. volume for volume.

**Liquor Calcis** (Lime-water),  $\text{Ca(OH)}_2 = \left\{ \begin{array}{l} 73.83 \\ *74 \end{array} \right.$ —

The U. S. P. directs lime-water to be estimated with *decinormal* oxalic acid V. S., using phenolphthalein as indicator.

Take 50 cc. of lime-water, add a few drops of phenolphthalein, and then carefully from a burette  $\frac{N}{10}$  oxalic acid V. S. until the red color is just discharged. 20 cc. of the  $\frac{N}{10}$  acid V. S. should be required for the neutralization. This corresponds to 0.14 (0.148) per cent. of calcium hydroxide.



Each cc. of  $\frac{N}{10}$  oxalic acid V. S. represents .0037 gm. of  $\text{Ca(OH)}_2$ .

Then  $.0037 \times 20 = 0.074 \text{ gm.}$

$$\frac{.074 \times 100}{50} = 0.148\%$$

**Syrupus Calcis, U. S. P.** (Liquor Calcis Saccharatus, Br. P.).—This is estimated in exactly the same way as the lime-water, except that the solution is weighed for analysis, not measured, as its specific gravity is much higher than that of water.

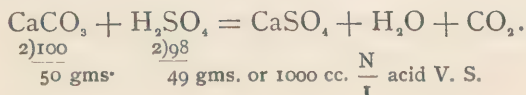
Operate upon about 25 grammes.

**Calcium Carbonate,  $\text{CaCO}_3$** ,  $= \left\{ \begin{array}{l} 99.76 \\ *_{100} \end{array} \right.$ .—No method is given for the estimation of calcium carbonate in the Pharmacopœia, but the following process may be used:

One gm. of calcium carbonate is mixed with 5 cc. of water. A measured excess of normal sulphuric acid V. S. is now added, and the solution boiled to drive off the  $\text{CO}_2$ . Then add a few drops of phenolphthalein T. S., and titrate with  $\frac{N}{I}$  alkali V. S. until a faint pink color is obtained.

Note the quantity of  $\frac{N}{I}$  alkali used, and deduct this from the quantity of  $\frac{N}{I}$  acid first added, and the amount of acid which combined with the calcium is obtained.

Each cc. of  $\frac{N}{I}$  acid V. S. represents .05 gm. of  $\text{CaCO}_3$ .



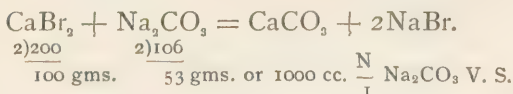


Assuming that 30 cc. of  $\frac{N}{I} H_2SO_4$  V. S. were added to the 1 gm. of  $CaCO_3$ , and that 11 cc. of  $\frac{N}{I} KOH$  V. S. were required to bring the mixture back to neutrality, then 19 cc. of  $\frac{N}{I} H_2SO_4$  were actually required to saturate the  $CaCO_3$ .

Therefore  $.05 \times 19 = .95$  gm., or 95%.

**Calcium Bromide**,  $CaBr_2 = \left\{ \begin{array}{l} 199.43 \\ *200 \end{array} \right.$ .—This salt when dissolved in water may be estimated directly with normal solution of sodium carbonate.

One gm. of the salt is dissolved in a small quantity of water. The solution is neutralized, if it is acid or alkaline, heated to boiling, a few drops of phenolphthalein T. S. added, and the solution titrated with  $\frac{N}{I}$  sodium carbonate V. S. delivered cautiously, with boiling, until the red color is permanent.

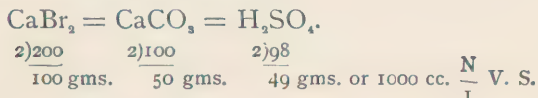


Each cc. of  $\frac{N}{I} Na_2CO_3$  V. S. represents 0.1 gm. of calcium bromide.

If 9 cc. are used, the salt contains  $0.1 \times 9 = .9$  gm., or 90%, of pure  $CaBr_2$ .

Another way is to add an excess of ammonium-carbonate solution with some free ammonia to the solution of calcium bromide, in order to precipitate all the base in the form of carbonate. The carbonate is then

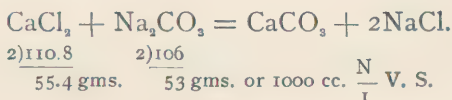
separated by filtration, thoroughly washed with hot water to remove all soluble matters, and then titrated as directed for carbonate.



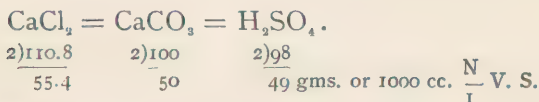
Each cc. of  $\frac{N}{I}$  acid thus represents 0.1 gm. of  $\text{CaBr}_2$ .

See U. S. P. method, page 103.

**Calcium Chloride**,  $\text{CaCl}_2 = \left\{ \begin{array}{l} 110.65 \\ *110.8 \end{array} \right.$ .—This salt may be estimated in exactly the same way as described for the bromide.



1 cc.  $\frac{N}{I} \text{Na}_2\text{CO}_3 = .0554 \text{ gm. of CaCl}_2.$



1 cc.  $\frac{N}{I} \text{H}_2\text{SO}_4 = .0554 \text{ gm. of CaCl}_2.$

**Barium Chloride**,  $\text{BaCl}_2$ , and **Barium Nitrate**,  $\text{Ba}(\text{NO}_3)_2$ .—These two salts are estimated in the same way as the soluble salts of calcium noted in the previous chapter.

The factor for  $\text{BaCl}_2$  is 0.10385 gm.,

the factor for  $\text{Ba}(\text{NO}_3)_2$  is 0.13045 gm.,

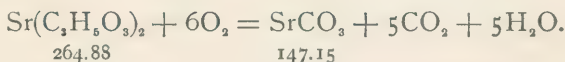
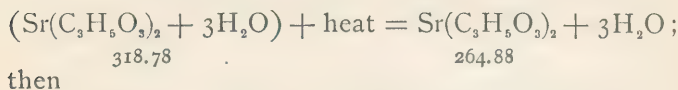
using normal volumetric solutions,

$$\text{Strontium Lactate, } \text{Sr}(\text{C}_3\text{H}_5\text{O}_3)_2 + 3\text{H}_2\text{O} = \begin{cases} 318.76 \\ *319.3 \end{cases}$$

—1.33 gms. of the salt, rendered anhydrous before being weighed, by careful drying at  $110^\circ \text{C}$ . ( $230^\circ \text{F}$ .), is ignited, until most of the carbon has disappeared, and then mixed with 10 cc. of water. A few drops of methyl-orange T. S. are now added, and the mixture titrated with  $\frac{\text{N}}{\text{I}} \text{H}_2\text{SO}_4$  V. S. until a faint red color is produced.

9.9 cc. of the  $\frac{\text{N}}{\text{I}}$  acid should be required, corresponding to 98.6% of the pure salt.

The first step in this process is to drive off the water of crystallization.



Thus

$$\begin{array}{ccc} \text{Sr}(\text{C}_3\text{H}_5\text{O}_3)_2 = \text{SrCO}_3 = \text{H}_2\text{SO}_4. & & \\ \begin{array}{r} 2)264.88 \\ \hline 132.44 \end{array} & \begin{array}{r} 2)147.15 \\ \hline 73.57 \end{array} & \begin{array}{r} 2)98 \\ \hline 49 \text{ gms. or } 1000 \text{ cc. } \frac{\text{N}}{\text{I}} \text{ acid V. S.} \end{array} \end{array}$$

Thus each cc. of  $\frac{\text{N}}{\text{I}} \text{H}_2\text{SO}_4$  represents 0.13244 gm. of pure anhydrous strontium lactate.

If 9.9 cc. are required, then

$$\begin{array}{l} 0.13244 \times 9.9 = 1.311156 \text{ gms.} \\ \frac{1.311156 \times 100}{1.33} = 98.6\% \end{array}$$

In this process, if the ignition is carried too far, the strontium carbonate is decomposed into strontium oxide.

Magnesium salts may be estimated by precipitating as ammonia-magnesian phosphate, and titrating this precipitate as directed for phosphoric acid.

## CHAPTER X.

## ANALYSIS BY PRECIPITATION.

THE general principle of this method is that the determination of the quantity of a given substance is effected by the formation of a precipitate, upon the addition of the standard solution to the substance under examination.

The end of the reaction is determined in three ways:

1. By adding the standard solution until no further precipitate occurs, as in the estimation of chlorides, etc., by silver nitrate.

2. By the use of an indicator. This may either be contained in the liquid under analysis; or used externally, by frequently bringing a portion of it in contact with a drop of the liquid during the titration.

The titration is continued until the slightest excess of the standard solution is shown by the production of a characteristic reaction with the indicator.

3. By adding the standard solution until a precipitate is produced, as in the estimation of cyanogen by standard silver solution.

The first of these endings can only be applied with accuracy to silver and chlorine estimations, as the silver chloride which is formed is almost perfectly insoluble and has a tendency to curdle closely by shaking, so as to leave a clear supernatant liquid.

Most of the other precipitates, such as barium sulphate, calcium oxalate, etc., although heavy and insoluble, do not readily and perfectly subside, because of their finely divided or powdery nature. They must therefore be excluded from this class.

In these cases, therefore, it is necessary to find an indicator which brings them into class 2.

The third class comprises only two processes, viz., the determination of cyanogen by silver, and that of chlorine by mercuric nitrate.

#### ESTIMATION OF HALOID SALTS.

The estimation of these salts is based upon the powerful affinity existing between the halogens and silver, and the ready precipitation of the resulting chloride, bromide, or iodide.

Standard solution of silver nitrate is used for this purpose, and for the sake of exactness and convenience is made of decinormal strength, and in many cases it is advisable to use centinormal solutions.

**The Decinormal  $\left(\frac{N}{10}\right)$  Silver Nitrate V. S.** is official.  $\text{AgNO}_3 = \left\{ \begin{array}{cc} 169.55 & 16.955 \\ *169.7 & 16.97 \end{array} \right\}$  gms. are contained in 1 litre.—Dissolve 16.97 gms. of pure silver nitrate in sufficient water to make, at or near  $15^\circ \text{C.}$  ( $59^\circ \text{F.}$ ), exactly 1000 cc. 1 litre of this solution thus contains  $\frac{1}{10}$  of the molecular weight in grammes of silver nitrate. It is therefore a decinormal solution.

If pure crystals of silver nitrate are not readily obtainable, and pure sodium chloride is at hand, a solution of the silver nitrate may be made of approximate

strength, a little stronger than necessary, and then standardized by means of the sodium chloride, as follows: 0.117 gm. of sodium chloride is dissolved in water, and a burette is filled with the solution of silver nitrate to be standardized. The silver solution is now slowly added from the burette to the sodium-chloride solution contained in a beaker until no more precipitate of silver chloride is produced.

If neutral potassium chromate is used as an indicator, the end of the reaction is shown by the appearance of yellowish-red silver chromate. This indication is extremely delicate. The silver nitrate does not act upon the chromate until all of the chloride is converted into silver chloride.

In the above reaction 20 cc. of silver nitrate should be required. But since the silver-nitrate solution is too strong, less of it will complete the reaction, and the solution must be diluted so that exactly 20 cc. will be required to precipitate the chlorine in 0.117 gm. of NaCl.

Thus if 17 cc. are used, each 17 cc. must be diluted to 20 cc., or each 170 cc. to 200 cc., or the entire remaining solution in the same proportion.

After dilution a fresh trial should always be made.

Nitrate of silver solution should be kept in dark amber-colored, glass-stoppered bottles, carefully protected from dust.

Titration by decinormal silver nitrate V. S. may be managed in various ways, adapted to the special preparation to be tested.

1. In most cases it is directed by the U. S. P. to be used in the presence of a small quantity of potassium chromate T. S.



2. In some cases it is added until the first appearance of a permanent precipitate, as in potassium cyanide and hydrocyanic acid.

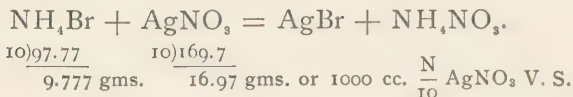
3. It may be used in all cases without an indicator by observing the exact point when no further precipitate occurs. But since this consumes too much time in waiting for the precipitate to subside, so as to render the supernatant liquid sufficiently clear to recognize whether a further precipitate is produced by the addition of the silver solution, it is impracticable. It may, however, be practised in the case of ferrous iodide, where the addition of potassium chromate T. S. would be improper, since it reacts with the iron.

4. It may be added in definite amount, known to be in excess of the quantity required, and the excess measured back by titration with decinormal potassium sulphocyanate V. S., or even with decinormal sodium chloride V. S. (residual titration).

In case an excess of the  $\frac{N}{10}$  silver nitrate V. S. is added accidentally, it is only necessary to add a definite volume of a  $\frac{N}{10}$  solution of the salt under examination, and finish the titration with  $\frac{N}{10}$  silver nitrate, deducting, of course, the same number of cc. of silver solution as has been added of the salt solution.

**Ammonium Bromide**,  $\text{NH}_4\text{Br} = \left\{ \begin{array}{l} 97.77 \\ *98 \end{array} \right. . - 3 \text{ grs.}$   
of the salt are dried at  $100^\circ \text{C.}$  ( $212^\circ \text{F.}$ ) and dissolved in water to the measure of 100 cc. 10 cc. of this solution are placed in a beaker, a few drops of potassium chromate T. S. added, and then the decinormal silver

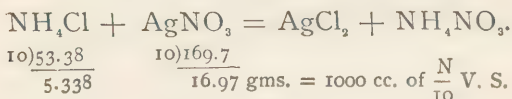
nitrate V. S. carefully added from a burette, until a permanent red coloration is produced. The red coloration is due to the formation of red chromate of silver, which takes place after all of the bromine has combined with the silver. Apply the equation :



Thus each cc. of the  $\frac{\text{N}}{10}$  V. S. represents .009777 gm. of  $\text{NH}_4\text{Br}$ .

The U. S. P. salt should require 30.9 cc. of  $\frac{\text{N}}{10}$   $\text{AgNO}_3$  V. S.

But as a rule this salt contains an impurity (ammonium chloride) which will be precipitated by the silver nitrate as well as the bromide. The presence of this impurity must therefore be taken into account in calculating the percentage of bromide.



The amount of the salt examined equivalent to 1000 cc. of  $\frac{\text{N}}{10}$  silver solution is first calculated by simple proportion :

$$30.9 \text{ cc.} : .3 \text{ gm.} :: 1000 \text{ cc.} : x. \qquad x = 9.708.$$

Then

$$9.777 - 9.708 = y. \qquad y = .069.$$

.069 = the excess of  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. used up by the ammonium chloride, reckoned in terms of bromide ( $\text{NH}_4\text{Br}$ ); and since 5.338 gms. of  $\text{NH}_4\text{Cl} = 9.777$  gms. of  $\text{NH}_4\text{Br}$ , the excess which  $\text{NH}_4\text{Cl}$  can consume is represented by  $9.777 - 5.338 = 4.439$ . Therefore, as

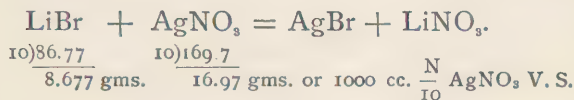
$$4.439 : 5.338 :: .069 : x. \quad x = 0.08297.$$

0.08297 = the amount of ammonium chloride present in  $x$  grammes of the sample taken.

Lastly, calculate the percentage by simple proportion:

$$9.708 : .0829 :: 100 : P. \quad P = 0.85\% \text{ of } \text{NH}_4\text{Cl}.$$

**Lithium Bromide,  $\text{LiBr}$**  =  $\left\{ \begin{array}{l} 86.77 \\ *87 \end{array} \right.$ .—Dissolve 0.3 gm. of dry lithium bromide in 10 cc. of water, add 2 drops of potassium chromate T. S., and then titrate with decinormal silver nitrate V. S. until a permanent red color of silver chromate makes its appearance. 0.3 gm. of the U. S. P. salt requires 33.5 cc. of  $\frac{N}{10}$  V. S.



Thus each cc. of  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. = 0.008677 gm. of pure lithium bromide.

**Potassium Bromide,  $\text{KBr}$**  =  $\left\{ \begin{array}{l} 118.79 \\ *119 \end{array} \right.$ .—Operate upon 0.1 gm. of the salt dissolved in about 10 cc. of

water. Add a few drops of potassium chromate T. S., and titrate with  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. until a permanent red color of silver chromate is produced. According to the U. S. P., 0.5 gm. of the well-dried salt should require 42.85 cc. of  $\frac{N}{10}$   $\text{AgNO}_3$  V. S.



$$\begin{array}{r} 10)118.79 \\ 11.879 \text{ gms.} \end{array} \quad \begin{array}{r} 10)169.7 \\ 16.97 \text{ gms.} \end{array} \quad \text{or } 1000 \text{ cc. } \frac{N}{10} \text{ AgNO}_3 \text{ V. S.}$$

Thus each cc. represents .011879 gm. of KBr. Potassium chloride is a common impurity; to calculate it, proceed as for  $\text{NH}_4\text{Cl}$ , 74.4 of  $\text{KCl}$  being equal to 118.79 of  $\text{KBr}$ .

**Sodium Bromide**,  $\text{NaBr} = \left\{ \begin{array}{l} 102.76 \\ *_{103} \end{array} \right.$ .—This salt is tested in exactly the same manner as the potassium bromide. A convenient quantity to operate upon is 0.1 gm.

The U. S. P. directs that 0.3 gm. of the well-dried salt be dissolved in 10 cc. of water, two drops of potassium chromate T. S. added, and the mixture titrated with decinormal silver nitrate V. S. until a permanent red color of silver chromate appears.

Note the number of cc. required to produce this effect, and multiply this number by the factor 0.010276 gm. This will give the quantity of  $\text{NaBr}$  present in the sample taken.

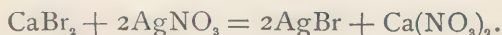
According to the U. S. P., not more than 29.8 cc. of the standard silver solution, corresponding to at least 97.29% of the pure salt, should be required.

The chloride which is present as an impurity may

be calculated in the same manner as ammonium chloride, 5.837 gms. of the chloride being equal to 10.276 gms. of sodium bromide.

**Calcium Bromide**,  $\text{CaBr}_2 \left\{ \begin{array}{l} 199.43 \\ *_{200} \end{array} \right.$ .—This salt may be tested as described on page 92.

The U. S. P. method is as follows: 0.25 gm. of the well-dried salt is dissolved in 10 cc. of water; 2 drops of potassium chromate T. S. are then added, and the solution titrated with decinormal silver nitrate V. S. until a permanent red color is produced. 25 cc. of the standard silver-nitrate solution should be required to produce this result, corresponding to 99.7% of the pure salt, a greater amount of the standard solution indicating the presence of calcium chloride, a smaller amount indicating other impurities.



$$\begin{array}{r} 2)199.43 \qquad 2)339.4 \\ 10)99.715 \qquad 10)169.7 \\ \hline 9.9715 \text{ gms.} \quad 16.97 \text{ gms. or } 1000 \text{ cc.} \end{array} \quad \frac{\text{N}}{10} \text{ AgNO}_3 \text{ V. S.}$$

Thus each cc. of  $\frac{\text{N}}{10} \text{ AgNO}_3$  V. S. represents .0099715 gm. of  $\text{CaBr}_2$ .

Therefore 25 cc. represent  $.0099715 \times 25 = 0.2492875$  gm.

$$\frac{.2492875 \times 100}{0.25} = 99.7\%$$

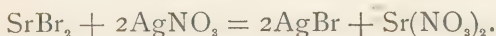
**Strontium Bromide**,  $\text{SrBr}_2 + 6\text{H}_2\text{O} = \left\{ \begin{array}{l} 354.58 \\ *_{355.3} \end{array} \right.$ .—

This salt is tested volumetrically, according to the U. S. P., in the following manner:

0.3 gm. of strontium bromide, rendered anhydrous by

thorough drying before being weighed, is dissolved in 10 cc. of water, 3 drops of potassium *dichromate* T. S. are added, and then the decinormal silver nitrate V. S. is poured in from a burette until all of the bromide has combined with the silver nitrate and a permanent red coloration is produced.

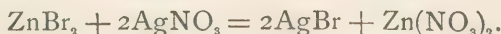
Not more than 24.6 cc. of decinormal silver nitrate V. S. should be required, corresponding to at least 98% of the pure salt.



$$\begin{array}{r} 2)246.82 \\ 10)123.41 \\ \hline 12.341 \text{ gms.} \end{array} \quad \begin{array}{r} 2)339.4 \\ 10)169.7 \\ \hline 16.97 \text{ gms.} \end{array} \quad \text{or } 1000 \text{ cc. } \frac{\text{N}}{10} \text{ AgNO}_3 \text{ V. S.}$$

Thus each cc. of  $\frac{\text{N}}{10} \text{ AgNO}_3$  V. S. represents 0.012341 gm. of strontium bromide.

**Zinc Bromide**,  $\text{ZnBr}_2 = \left\{ \begin{array}{l} 224.62 \\ *225 \end{array} \right.$ .—This salt is estimated as follows: 0.3 gm. of the dry salt is dissolved in 10 cc. of water, 2 drops of potassium chromate T. S. are added, and then decinormal silver nitrate V. S. is poured in from a burette until all of the bromide has combined with silver nitrate, and a permanent red color is produced. Note the number of cc. of the standard silver solution used, and multiply this number by the factor shown by the following equation, to obtain the amount of pure zinc bromide in the quantity taken:



$$\begin{array}{r} 20)224.62 \\ 11.231 \text{ gms.} \end{array} \quad \begin{array}{r} 20)339.4 \\ 16.97 \text{ gms.} \end{array} \quad \text{or } 1000 \text{ cc. } \frac{\text{N}}{10} \text{ AgNO}_3 \text{ V. S.}$$

Thus each cc. represents .011231 gm. of pure  $\text{ZnBr}_2$ . The U. S. P. salt should require 26.7 cc. of decinormal silver nitrate V. S. to produce the desired reaction, corresponding to not less than 99.95% of the pure salt.

Thus  $0.011231 \times 26.7 = 0.2998677$  gm.

$$\frac{0.2998677 \times 100}{0.3} = 99.95\%.$$

**Potassium Iodide, KI** =  $\left\{ \begin{array}{l} 165.56 \\ *165.5 \end{array} \right.$ .—This is estimated, according to the U. S. P., in a manner similar to the haloid salts just considered.

0.5 gm. of the well-dried salt is dissolved in 10 cc. of water, 2 drops of neutral potassium chromate T. S. are added, and then the  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. slowly added from a burette until a permanent red color of silver chromate is produced. Not more than 30.25 cc. nor less than 30 cc. of decinormal silver nitrate V. S. should be required. This quantity corresponds to 99.5% of the pure salt.



$$\begin{array}{r} 10)165.56 \\ 16.556 \text{ gms.} \end{array} \quad \begin{array}{r} 10)169.7 \\ 16.97 \text{ gms.} \end{array} \quad \text{or } 1000 \text{ cc. } \frac{N}{10} \text{ AgNO}_3 \text{ V. S.}$$

Each cc. of  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. thus corresponds to 0.016556 gm. of potassium iodide.

Thus  $0.016556 \times 30 = 0.49668$  gm.

$$\frac{0.49668 \times 100}{0.5} = 99.3\%$$



Potassium iodide may also be estimated volumetrically by  $\frac{N}{20}$  mercuric chloride V. S., the termination of the operation being indicated by the formation of a red precipitate.



This process originated with M. Personne, and is founded on the fact that if a solution of mercuric chloride be added to one of potassium iodide, in the proportion of one equivalent of mercuric chloride to four of potassium iodide, red mercuric iodide is formed, which dissolves at once to a colorless solution. The slightest excess of mercuric chloride will cause a brilliant red precipitate to make its appearance,  $HgI_2$ .



$$\begin{array}{r} 20)662.24 \\ \hline 33.112 \text{ gms.} \end{array} \quad \begin{array}{r} 20)270.54 \\ \hline 13.527 \text{ gms. or 1000 cc. of standard solution.} \end{array}$$

Thus each cc. of standard solution of the above strength represents 0.033112 gm. of potassium iodide, which means that 1 cc. is the largest quantity of this standard solution which can be added to 0.033112 gm. of potassium iodide without producing a permanent precipitate.

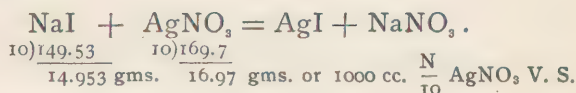
The above solution of mercuric chloride is not strictly a  $\frac{N}{20}$  V. S. Potassium iodide is a univalent salt; and since four molecules of it are precipitated by one molecule of mercuric chloride, the latter is chemically equivalent to four atoms of hydrogen; and  $\frac{1}{4}$  of its

molecular weight in grammes, dissolved in water to one litre, is a normal solution, and  $\frac{1}{20}$  of this is a  $\frac{N}{20}$  V. S.

The author of this process states that neither chlorides, bromides, nor carbonates interfere with the reaction.

**Sodium Iodide**,  $\text{NaI} = \left\{ \begin{array}{l} 149.53 \\ *149.5 \end{array} \right.$ .—Dissolve 0.5 gm. of the well-dried salt in 10 cc. of water, add 2 drops of potassium chromate T. S., and then pass into the solution from a burette  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. until a permanent red coloration is produced.

Note the number of cc. used, and multiply this by the factor.



Each cc. of  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. represents 0.014953 gm. of NaI.

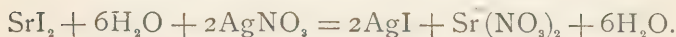
Assuming that 33.4 cc. of  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. were required, each representing 0.014953 gm. of NaI, then the quantity tested contained

$$\begin{array}{l} 33.4 \times 0.014953 \text{ gm. or } 0.4994302 \text{ gm.} \\ \frac{0.4994302 \times 100}{0.5} = 99.8\% \end{array}$$

The U. S. P. requirement is that the salt contain 98%, at least, of pure Na.

**Strontium Iodide**,  $\text{SrI}_2 + 6\text{H}_2\text{O} = \left\{ \begin{array}{l} 448.12 \\ *448.3 \end{array} \right. \cdot 0.3$  gm. of strontium iodide, rendered anhydrous before being weighed, is dissolved in 10 cc. of water, 3 drops of potassium dichromate T. S. are then added, and the  $\frac{\text{N}}{10}$   $\text{AgNO}_3$  V. S. run in from a burette until a permanent red coloration is produced.

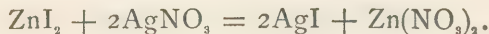
Apply the following equation:



$$\begin{array}{r} 2)448.12 \\ 10)224.06 \\ \hline 22.406 \text{ gms.} \end{array} \qquad \begin{array}{r} 2)339.4 \\ 10)169.7 \\ \hline 16.97 \text{ gms. or 1000 cc.} \end{array} \quad \frac{\text{N}}{10} \text{AgNO}_3 \text{ V. S.}$$

This equation shows that each cc. of the  $\frac{\text{N}}{10}$   $\text{AgNO}_3$  V. S. represents 0.022406 gm. of  $\text{SrI}_2$ .

**Zinc Iodide**,  $\text{ZnI}_2 = \left\{ \begin{array}{l} 318.16 \\ *318 \end{array} \right. \cdot$ —Dissolve 0.5 gm. of dry zinc iodide in 10 cc. of water, add 2 drops of potassium chromate T. S., and then run into the mixture from a burette  $\frac{\text{N}}{10}$   $\text{AgNO}_3$  V. S. until a permanent red color is produced, indicating that all of the iodide has been precipitated in the form of silver iodide. Each cc. of the  $\frac{\text{N}}{10}$  silver solution used represents 0.015908 gm. of zinc iodide.



$$\begin{array}{r} 2)318.16 \\ 10)159.08 \\ \hline 15.908 \text{ gms.} \end{array} \qquad \begin{array}{r} 2)339.4 \\ 10)169.7 \\ \hline 16.97 \text{ gms. or 1000 cc.} \end{array} \quad \frac{\text{N}}{10} \text{AgNO}_3 \text{ V. S.}$$

The U. S. P. directs that not less than 31 cc. nor more than 31.4 cc. of  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. be required to produce the desired result, 31 cc. corresponding to 98.62% and 31.4 cc. to 99.9% of pure zinc iodide.

$$0.015908 \times 31.4 = 0.4995112 \text{ gm. of } \text{ZnI}_2.$$

Then

$$\frac{0.4995112 \times 100}{0.5} = 99.9\%$$

**Ammonium Chloride**,  $\text{NH}_4\text{Cl} = \left\{ \begin{array}{l} 53.38 \\ *53.4 \end{array} \right.$ .—It is estimated in the same manner as the other soluble haloid salts. A weighed quantity of the salt is dissolved in a small quantity of water and the solution titrated with  $\frac{N}{10}$  silver-nitrate solution until no more precipitation takes place, or, if potassium chromate T. S. has been added as indicator, until a red color makes its appearance.



$$\begin{array}{r} 10)53.38 \\ 5.338 \text{ gms.} \end{array} \quad \begin{array}{r} 10)169.7 \\ 16.97 \text{ gms. or } 1000 \text{ cc.} \end{array} \quad \frac{N}{10} \text{ V. S.}$$

Thus each cc. of  $\frac{N}{10}$  V. S. used represents 0.005338 gm. of  $\text{NH}_4\text{Cl}$ .

**Potassium Chloride**,  $\text{KCl} = \left\{ \begin{array}{l} 74.40 \\ *74.40 \end{array} \right.$ .—This is estimated in the same manner as the above, applying the following equation :



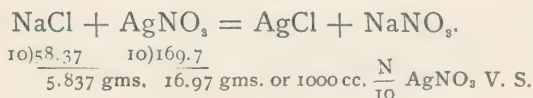
$$\begin{array}{r} 10)74.4 \\ 7.44 \text{ gms.} \end{array} \quad \begin{array}{r} 10)169.7 \\ 16.97 \text{ gms. or } 1000 \text{ cc.} \end{array} \quad \frac{N}{10} \text{ AgNO}_3 \text{ V. S.}$$

Thus each cc. of  $\frac{N}{10}$  V. S. represents 0.00744 gm. of KCl.

**Sodium Chloride**,  $\text{NaCl} = \left\{ \begin{array}{l} 58.37 \\ *58.4 \end{array} \right.$ .—A weighed quantity of the well-dried salt, say 0.2 gm., is dissolved in about 10 cc. of water and the solution mixed with a few drops of potassium chromate T. S. Then  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. is run in from a burette until all the chloride is precipitated and a permanent red color of silver chromate is produced.

The U. S. P. directs that 0.195 gm. of the salt should require not less than 33.4 cc. of  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. to produce this reaction.

The following equation shows the reaction which takes place between the sodium chloride and the silver nitrate :



Each cc. of the standard solution thus represents 0.005837 gm. of NaCl.

$$.005837 \times 33.4 = 0.194958 \text{ gm. of NaCl.}$$

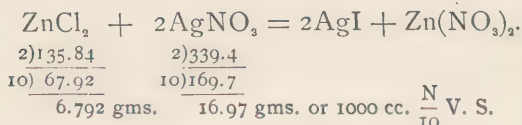
$$\frac{0.194958 \times 100}{0.195} = 99.9\%$$

**Zinc Chloride**,  $\text{ZnCl}_2 = \left\{ \begin{array}{l} 135.84 \\ *135.8 \end{array} \right.$ .—This salt is tested in exactly the same way as the other haloid salts.

Dissolve 0.3 gm. of the dry salt in about 10 cc. of water, add a few drops (2 drops) of potassium chromate T. S., and then run into the mixture from a burette,  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. until a permanent red color is produced.

It should require 44.1 cc. of the standard silver solution to produce this result.

The reaction is shown by the following equation :



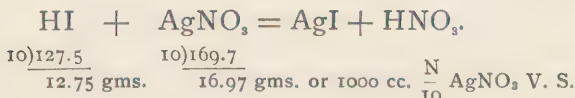
Thus it is seen that each cc. of the  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. represents 0.006792 gm. of  $\text{ZnCl}_2$ .

$$0.006792 \times 44.1 = 0.2995272 \text{ gm.}$$

$$\frac{0.2995272 \times 100}{0.3} = 99.84\%$$

The U. S. P. requires 99.84%.

**Syrupus Acidi Hydriodici**, a syrupy liquid containing about 1% of HI U. S. P.  $\text{HI} = \left\{ \begin{array}{l} 127.53 \\ *127.5 \end{array} \right.$ .—Operate upon 15 grammes. The reaction which occurs is as follows :



The end of the reaction is shown by the cessation of the formation of a precipitate.

Since nitric acid is liberated, potassium chromate is not admissible as indicator.

The U. S. P. directs that the syrup be neutralized by ammonia water before titration. This prevents the formation of nitric acid, and admits of the use of potassium chromate as indicator.

(31.875) \*32 gms. of the syrup, neutralized, and mixed with 2 drops of the indicator, should require 25 cc. of decinormal silver-nitrate solution to produce a permanent red tint.

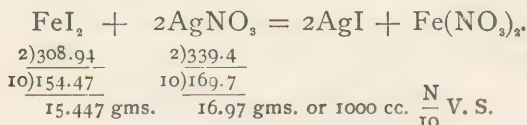
Each cc. represents 0.01275 gm. of HI.

$$0.01275 \times 25 = 0.31875 \text{ gm.}$$

$$\frac{0.31875 \times 100}{31.875} = 1\%$$

**Syrupus Ferri Iodidi**, a syrup containing about 10% by weight of ferrous iodide ( $\text{FeI}_2$ ) U. S. P.  $\text{FeI}_2 =$   
 $\left\{ \begin{array}{l} 308.94 \\ *309 \end{array} \right.$ —Take 2 gms. of the syrup, mix it with a

small quantity of water, and run in the  $\frac{\text{N}}{10}$  silver solution. The close of the reaction is shown by the cessation of the formation of a precipitate. Potassium chromate is not admissible as an indicator in this case.



Thus each cc. represents 0.015447 gm. of ferrous iodide.

*The U. S. P. method* originated with Volhard. It has the advantage over the direct method for haloids



with chromate indicator, in that it may be used in the presence of nitric acid. It thus enables the haloids to be estimated in the presence of a phosphate or other salt which precipitates silver in a neutral, but not in an acid solution.

It depends upon entirely precipitating the chloride, in the presence of nitric acid, by a known excess of standard solution of silver nitrate, and then estimating the excess of silver left uncombined, by the aid of a standard solution of potassium sulphocyanate, using ferric alum as an indicator.

The sulphocyanate has a greater affinity for silver than it has for iron, and therefore so long as any silver is in solution, the sulphocyanate will combine with it and form a precipitate of silver sulphocyanate.

As soon as the silver is all taken up, the sulphocyanate will combine with the ferric alum and strike a brownish-red color.

The sulphocyanate solution is to be made of such strength that it corresponds with the silver solution, volume for volume.

The difference between the volume of silver solution originally added, and the volume of sulphocyanate solution used, will give the volume of silver solution equivalent to the haloid salt present.

**Decinormal Potassium Sulphocyanate V. S.** (Volhard's Solution),  $\text{KSCN} = \left\{ \begin{array}{cc} 96.99 & 9.699 \\ *97 & *9.7 \end{array} \right\}$  gms. in

1 litre.—Dissolve 10 gms. of pure crystallized potassium sulphocyanate (thiocyanate) in 1000 cc. of water.

This solution, which is too concentrated, must be adjusted so as to correspond in strength exactly with decinormal silver nitrate V. S. For this purpose in-

Introduce into a flask 10 cc. of  $\frac{N}{10}$   $\text{AgNO}_3$  V. S., 0.5 cc. of ammonio-ferric sulphate T. S., and 5 cc. of diluted nitric acid.

Run into this mixture from a burette the sulphocyanate solution.

At first a white precipitate of silver sulphocyanate is produced, giving the fluid a milky appearance, and then, as each drop of sulphocyanate falls in, it is surrounded by a deep brownish-red cloud of ferric sulphocyanate, which quickly disappears on shaking, as long as any of the silver nitrate remains unchanged.

When the point of saturation is reached and the silver has all been precipitated, a single drop of the sulphocyanate solution produces a faint brownish-red color, which does not disappear on shaking.

Note the number of cc. of the sulphocyanate solution used, and dilute the whole of the remaining solution so that equal volumes of this and of the decinormal silver nitrate V. S. will be required to produce the permanent brownish-red tint. (The same tint of brown or red to which the volumetric solution is adjusted must be attained when the solution is used in volumetric testing.)

Assuming that 9.5 cc. of the sulphocyanate solution were required to produce the reaction, then each 9.5 cc. must be diluted to make 10 cc., or the whole of the remaining solution in the same proportion.

Always make a new trial after the dilution to see if the solutions correspond.

The U. S. P. method for estimating *syrup of ferrous iodide* is as follows:

1.5447 gms. (\*1.55 gms.) of the syrup and 10 cc. of

water are introduced into a flask, 11 cc. of decinormal silver nitrate V. S. are added, then 5 cc. of diluted nitric acid, and 5 cc. of ferric ammonium sulphate T. S. The decinormal potassium sulphocyanate V. S. is now run into the mixture from a burette until a reddish-brown tint is produced, which does not disappear upon shaking. Not more than 1 cc. should be required.

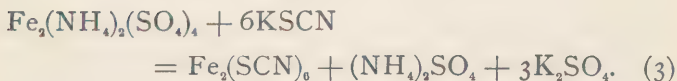
This corresponds to 10% of ferrous iodide. The reactions which take place are shown by the following equations:



15.447 gms. 16.97 gms. or 1000 cc.  $\frac{N}{10}$  AgNO<sub>3</sub> V. S.



16.97 gms. 9.699 gms. or 1000 cc.  $\frac{N}{10}$  KSCN V. S.



The  $\text{Fe}_2(\text{SCN})_6$  gives the brownish-red color to the solution.

The object of the nitric acid is to acidulate the solution, facilitate the precipitation of the silver, and to oxidize the ferrous nitrate.

In the above case 11 cc. of silver nitrate are originally added. If 1 cc. of potassium sulphocyanate be required, it shows that 1 cc. of the silver-nitrate solution was in excess, and that 10 cc. went into combination with the ferrous iodide. The equation shows us that

each cc. of silver nitrate V. S. represents 0.015447 gm. of ferrous iodide ; then 10 cc. represent

$$0.015447 \times 10 = 0.15447 \text{ gm.,}$$

$$\text{and } \frac{.15447 \times 100}{1.5447} = 10\%$$

of  $\text{FeI}_2$  in the U. S. P. syrup.

**Saccharated Ferrous Iodide.**—The process for estimating this compound is exactly the same as that for syrup of ferrous iodide.

1.5447 gms. (\*1.55 gms.) of the saccharated ferrous iodide are dissolved in about 20 cc. of water in a small flask, and to this solution is added first 22 cc. of  $\frac{\text{N}}{10}$   $\text{AgNO}_3$  V. S., then 5 cc. of diluted nitric acid, and

5 cc. of ferric ammonium sulphate T. S. The  $\frac{\text{N}}{10}$   $\text{KSCN}$  V. S. is then run in, from a burette, until the reddish-brown color of ferric sulphocyanate is produced.

Not more than 2 cc. of the  $\frac{\text{N}}{10}$   $\text{KSCN}$  V. S. should be required.

This corresponds to 20% of pure ferrous iodide.

$$22 \text{ cc. of } \frac{\text{N}}{10} \text{ silver nitrate}$$

$$- \underline{2} \text{ cc. of } \frac{\text{N}}{10} \text{ potassium sulphocyanate}$$

$$= 20 \text{ cc. of } \frac{\text{N}}{10} \text{ silver nitrate,}$$

which reacted with the ferrous iodide, then

$$0.015447 \times 20 = 0.30894 \text{ gm.,}$$

$$\frac{0.30894 \times 100}{1.5447} = 20\%$$

**Syrup of Ferrous Bromide**, U. S. P. 1880,  $\text{FeBr}_2 = \left\{ \begin{array}{l} 215.4 \\ *216 \end{array} \right.$ .—This syrup may be tested in the same manner as the syrup of ferrous iodide, either by the direct method, using the cessation of precipitation as the end reaction, or by the residual method with potassium sulpho-cyanate.

The factor is 0.01077.

**Hydrocyanic Acid**,  $\text{HCN} = \left\{ \begin{array}{l} 26.98 \\ *27 \end{array} \right.$ .—Dilute hydrocyanic acid may be estimated by weighing out about 5 gms., and adding to this sufficient soda or potassa solution to convert the acid into sodium or potassium cyanide ( $\text{NaCN}$  or  $\text{KCN}$ ), and leave the solution strongly alkaline.

To this solution is added the decinormal silver-nitrate solution until a permanent turbidity occurs.

This turbidity is due to the precipitation of silver cyanide, and affords a delicate proof of the completion of the reaction.

The difficulty experienced in this process is in the conversion of the acid into the cyanide. The sodium cyanide has a strong alkaline reaction, turning litmus blue when only a small proportion of the acid has been neutralized.

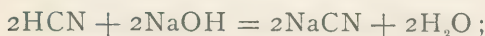
If the titration is conducted before the acid is completely neutralized, that which is free will not be acted

upon. Indeed, cyanide of sodium may be estimated in the presence of hydrocyanic acid in this way.

According to Senier, the following procedure will answer well :

To the dilute hydrocyanic acid add soda solution to a strong alkaline reaction, determined by litmus tincture. Then titrate with  $\frac{N}{10}$  silver nitrate V. S., drop by drop, from the burette. If the liquid becomes acid, add a little more soda solution to bring it back to alkalinity, and continue the titration until the turbidity indicates the end of the reaction. The liquid must be kept alkaline throughout the process. It is not well to add too much soda solution at the beginning, as this would use up too much of the silver solution, and make the reading a trifle too high.

The following equations, etc., explain the reactions :



$$\begin{array}{r} 10)53.96 \\ \hline 5.396 \text{ gms.} \end{array}$$

$$\begin{array}{r} 10)97.96 \\ \hline 9.796 \text{ gms.} \end{array}$$



$$\begin{array}{r} 10)97.6 \\ \hline 9.796 \text{ gms.} \end{array} \quad \begin{array}{r} 10)169.7 \\ \hline 16.97 \text{ gms. or } 1000 \text{ cc.} \end{array} \quad \frac{N}{10} \text{ V. S.}$$

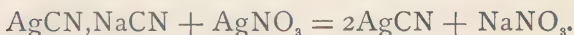
It is seen that 5.396 gms. of real HCN are equivalent to 9.796 gms. of sodium cyanide, and represent 16.97 gms. of silver nitrate, or 1000 cc. of the  $\frac{N}{10}$  V. S. That is, 1000 cc. of the  $\frac{N}{10}$   $\text{AgNO}_3$  V. S. may be added to a solution containing 9.796 gms. of sodium cyanide, and

no precipitate be produced; but if one or two drops more of the standard solution be added, a precipitate is at once formed.

Each cc. of  $\frac{N}{10}$   $\text{AgNO}_3$  V. S., which fails to produce a precipitate with a solution of sodium cyanide, represents 0.009796 gm. of  $\text{NaCN}$ , which is equivalent to .005396 gm. of  $\text{HCN}$ .

With 2 molecular weights of sodium or potassium cyanide, one molecule of silver nitrate forms a double salt, having the composition  $\text{NaCN}, \text{AgCN}$ , and which is soluble.

When more silver-nitrate solution is added, this soluble double salt is decomposed, and a precipitate of silver cyanide occurs, thus:



The U. S. P. method is as follows:

A weighed quantity of the acid is mixed with sufficient of an aqueous suspension of magnesia to make an opaque and decidedly alkaline mixture.

To this a few drops of potassium chromate T. S. are added, and the  $\frac{N}{10}$  silver solution delivered from a burette until the red color of silver chromate appears.

1.35 gms. of the diluted acid is mixed with enough water and magnesia to make an opaque mixture of about 10 cc. Add to this 2 or 3 drops of potassium chromate T. S., and then from a burette deliver the decinormal silver nitrate V. S. until a red tint is produced which does not again disappear by shaking.



Each cc. of the standard silver solution used, represents 0.002698 gm. of absolute HCN.



$$\begin{array}{r} 10)26.98 \\ \hline 2.698 \text{ gms.} \end{array} \quad \begin{array}{r} 10)169.7 \\ \hline 16.97 \text{ gms. or } 1000 \text{ cc.} \end{array} \frac{\text{N}}{10} \text{ silver nitrate V. S.}$$

**Potassium Cyanide, KCN** =  $\left\{ \begin{array}{l} 65.01 \\ *65 \end{array} \right.$ .—This salt may be estimated in the following manner :

1 gm. of the salt is dissolved in sufficient water, and into the solution, is delivered in drops the standard silver solution until a precipitate appears which is not redissolved on agitation.

If 0.65 gm. of KCN are taken, not less than 45 cc. of  $\frac{\text{N}}{10}$   $\text{AgNO}_3$  V. S. should be required.



$$\begin{array}{r} 10)130.02 \\ \hline 13.002 \text{ gms.} \end{array} \quad \begin{array}{r} 10)169.7 \\ \hline 16.97 \text{ gms. or } 1000 \text{ cc.} \end{array} \frac{\text{N}}{10} \text{ AgNO}_3 \text{ V. S.}$$

Thus each cc. of the standard silver solution represents 0.013 gm. of KCN.

$$\begin{array}{l} 0.013 \times 45 = 0.585 \text{ gm.} \\ \frac{.585 \times 100}{.65} = 90\% \end{array}$$

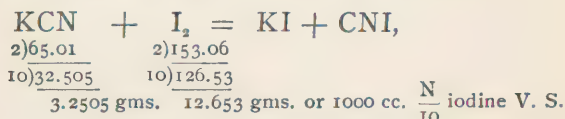
Cyanides may be estimated also by iodine, according to Fordos and Gelis.

This process depends upon the fact that potassium cyanide decolorizes iodine, potassium iodide and cyanogen iodide being formed.

When iodine solution is added to a solution of po-

tassium cyanide, the iodine is decolorized as long as there is any undecomposed cyanide present.

The following equation expresses the reaction



Thus each cc. of the volumetric solution represents 0.00325 gm. of KCN.

The end of the reaction is known by the yellow color of the iodine solution becoming permanent.

**Silver Nitrate**, (Argenti Nitras)  $\text{AgNO}_3 = \left\{ \begin{array}{l} 169.55 \\ *169.7 \end{array} \right.$

—Nitrate of silver and other salts of this metal may be volumetrically estimated by standard solution of sodium chloride.

The silver salt is dissolved in sufficient water in a beaker, and a decinormal volumetric solution of sodium chloride run in until a precipitate is no longer produced.

The estimation may also be performed by retitration as follows :

To the silver solution contained in a beaker add a measured excess of  $\frac{\text{N}}{10}$  sodium chloride V. S., and then, after adding a few drops of potassium chromate T. S., titrate the mixture with  $\frac{\text{N}}{10}$  silver nitrate V. S. until a permanent red color appears. Deduct the number of cc. of silver nitrate V. S. from the quantity of sodium chloride V. S. and the quantity of the latter is obtained which actually combined with the silver solution under examination.

The sulphocyanate method of Volhard may also be employed in the estimation of silver.

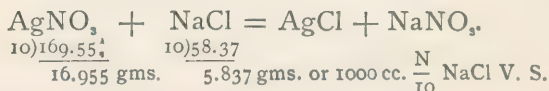
$\frac{N}{10}$  Sodium Chloride V. S.,  $\text{NaCl} = \left\{ \begin{array}{l} 58.37 \\ *58.4 \end{array} \right.$   
 $\left. \begin{array}{l} 5.837 \\ *5.84 \end{array} \right\}$  gms. in 1 litre.—Dissolve 5.837 gms. of pure sodium chloride in enough water to make exactly 1000 cc. at the ordinary temperature of the atmosphere.

Check this solution with decinormal silver nitrate V. S. The two solutions should correspond, volume for volume.

*Pure Sodium Chloride* may be prepared by passing into a saturated aqueous solution of the purest commercial chloride of sodium a current of dry hydrochloric-acid gas. The crystalline precipitate is then separated and dried at a temperature sufficiently high to expel all traces of free acid.

The U. S. P. method for silver nitrate is as follows:

\*0.34 gm. (0.3391 gm.) of silver nitrate is dissolved in 10 cc. of distilled water, and the solution carefully titrated with  $\frac{N}{10}$  NaCl V. S. until precipitation ceases. 20 cc. of the standard solution should be required.



Each cc. of the standard solution represents 0.016955 gm. of pure  $\text{AgNO}_3$ .

$$\begin{array}{l} 0.016955 \times 20 = 0.3391 \text{ gm.} \\ \frac{0.3391 \times 100}{.3391} = 100\% \end{array}$$

**Argenti Nitras Dilutus** (Mitigated Caustic).—This may be estimated in the same manner as the above.

The U. S. P. method is as follows :

1 gm. is dissolved in 10 cc. of distilled water, to this is added 20 cc. of  $\frac{N}{10}$  NaCl V. S. and a few drops of potassium chromate T. S., and the excess of  $\frac{N}{10}$  NaCl V. S. found by titration with  $\frac{N}{10}$  AgNO<sub>3</sub> V. S. until a permanent red color is produced. Not more than 0.5 cc. of the latter should be required. This indicates that 19.5 cc. of  $\frac{N}{10}$  NaCl V. S. were actually required to completely precipitate the silver nitrate tested.

Therefore

$$\begin{aligned} 0.016955 \times 20 &= .3306225 \text{ gm.} \\ \frac{.3306225 \times 100}{1} &= 33.06\% \end{aligned}$$

**Argenti Nitras Fusus** (Moulded Silver Nitrate. Lunar Caustic).—This is treated in exactly the same manner as the above. 0.34 gm. of the lunar caustic is dissolved in water, and 20 cc. of standard sodium chloride added; not more than 1 cc. of this should be in excess, as shown by retitration with silver nitrate V. S., using chromate indicator.

This corresponds to about 95% of pure silver nitrate.

**Silver Oxide**, Ag<sub>2</sub>O = 231.28.—May be converted into nitrate by solution in nitric acid, and then testing as above for silver nitrate. There will probably be some free nitric acid present if this is done,

and therefore the sulphocyanate method is best employed.

**The Sulphocyanate Method.**—A weighed quantity of the silver salt is dissolved in water, some diluted nitric acid and ammonium ferric sulphate solution are added, and the mixture then titrated with  $\frac{N}{10}$  potassium sulphocyanate V. S. until a permanent reddish-brown color of feric sulphocyanate is produced.

The following equation explains the reactions :



$$\begin{array}{r} 10)169.55 \\ \hline 16.955 \text{ gms.} \end{array} \quad \begin{array}{r} 10)96.99 \\ \hline 9.699 \text{ gms. or } 1000 \text{ cc. standard V. S.} \end{array}$$

Thus each cc. of the standard V. S. represents 0.016955 gm. of pure silver nitrate, or 0.010766 gm. of metallic silver.

**Liquor Plumbi Subacetatis** (Goulard's Extract).—This is an aqueous solution containing about 25% of lead subacetate, the formula of which is approximately  $\text{Pb}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_2 = 546.48$ . This is estimated by precipitation with sulphuric acid.

(13.6622 gms.) \*13.67 gms. of the solution are diluted with 50 cc. of water, a few drops of methyl-orange added, and the mixture titrated with normal sulphuric acid until the lead is completely precipitated and the mixture has assumed a red color. The red color indicates an acid reaction. The reaction is illustrated by the following equation :



$$\begin{array}{r} 4)546.48 \\ \hline 136.62 \text{ gms.} \end{array} \quad \begin{array}{r} 4)196 \\ \hline 49 \text{ gms. or } 1000 \text{ cc. } \frac{N}{1} \text{ H}_2\text{SO}_4 \text{ V. S.} \end{array}$$

Thus each cc. of  $\frac{N}{1}$   $H_2SO_4$  V. S. represents 0.13662 gm. of the subacetate.

If 25 cc. of the standard solution are required, then the solution under analysis contains  $0.13662 \times 25 = 3.4155$  gms.

$$\frac{3.4155 \times 100}{13.662} = 25\%$$

The Diluted Solution of Lead Subacetate (Lead Water) may be estimated in the same manner.

TABLE OF SUBSTANCES ESTIMATED BY PRECIPITATION, GIVING  
FORMULA, MOLECULAR WEIGHT, STANDARD  
SOLUTION USED, AND FACTOR.

Name.	Formula.	Molecular weight.	Standard Solution Used.	Factor.
Acid hydrobromic.....	HBr	80.76	$\frac{N}{10}$ AgNO <sub>3</sub>	0.008076
" hydrocyanic.....	HCN	26.98	$\frac{N}{10}$ AgNO <sub>3</sub>	0.002698
" hydriodic .....	HI	127.53	"	0.01275
Ammonium bromide.....	NH <sub>4</sub> Br	97.77	"	0.009777
" chloride.....	NH <sub>4</sub> Cl	53.38	"	0.005338
" iodide.....	NH <sub>4</sub> I	144.54	"	0.014454
Calcium bromide.....	CaBr <sub>2</sub>	199.43	"	0.0099715
" chloride.....	CaCl <sub>2</sub>	110.65	"	0.005532
Ferrous bromide.....	FeBr <sub>2</sub>	215.40	"	0.01077
" iodide.....	FeI <sub>2</sub>	308.94	$\frac{N}{10}$ AgNO <sub>3</sub> and $\frac{N}{10}$ KSCN	0.015447
Lead acetate. . . . .	Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	378.0	$\frac{N}{10}$ H <sub>2</sub> SO <sub>4</sub>	0.189
" subacetate.....	Pb <sub>2</sub> O(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	546.48	"	0.13662
Lithium bromide ....	LiBr	86.77	$\frac{N}{10}$ AgNO <sub>3</sub>	0.008677
Potassium bromide.....	KBr	118.79	"	0.011879
" chloride.....	KCl	74.40	"	0.00744
" cyanide.....	KCN	65.01	"	0.01300
" iodide.....	KI	165.56	"	0.016556
" sulphocyanide	KSCN	96.99	"	0.009699
Silver (metallic).....	Ag <sub>2</sub>	215.32	$\frac{N}{10}$ NaCl or $\frac{N}{10}$ KSCN	0.010766
" nitrate.....	AgNO <sub>3</sub>	169.55	"	0.016955
" oxide .....	Ag <sub>2</sub> O	231.28	"	0.011564
Sodium bromide.....	NaBr	102.76	$\frac{N}{10}$ AgNO <sub>3</sub>	0.010276
" chloride.....	NaCl	58.37	"	0.005837
" iodide.....	NaI	149.53	"	0.014953
Strontium bromide.. .	SrBr <sub>2</sub> ·6H <sub>2</sub> O	354.58	"	0.012341
" iodide.....	SrI <sub>2</sub> ·6H <sub>2</sub> O	448.12	"	0.022406
Zinc bromide.....	ZnBr <sub>2</sub>	224.62	"	0.011231
" chloride.....	ZnCl <sub>2</sub>	135.84	"	0.006792
" iodide.....	ZnI <sub>2</sub>	318.16	"	0.015908



## CHAPTER IX.

## OXIDIMETRY—ANALYSIS BY OXIDATION.

AN extensive series of analyses are made by this method, with extremely accurate results—in fact, the results are generally more accurate than any which can be obtained by weighing.

The principle involved in this method is extremely simple.

Substances which are capable of absorbing oxygen or are susceptible of an equivalent action are subjected to the action of an oxidizing agent of known power, and the quantity of the latter required for complete oxidation ascertained.

The substances which are used as oxidizing agents in volumetric analysis are potassium dichromate, potassium permanganate, iodine, etc.

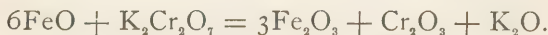
The reducing agents, or deoxidizers, are sodium thio-sulphate, oxalic acid, arsenous oxide, stannous chloride, metallic zinc, and magnesium.

Thus ferrous oxide ( $\text{FeO}$ ), an oxidizable substance, is ever ready and willing to take up oxygen, while potassium dichromate and permanganate are always ready to give up some of their oxygen. When potassium permanganate gives up its oxygen in this way it loses its color, and in volumetric analysis advantage is taken of this fact. When the permanganate, which is added in drops from a burette, is no longer decolor-

ized, the iron salt is completely oxidized. The reaction is as follows :



The oxidation of ferrous oxide by potassium dichromate is shown by the following equation :



An oxidation is always accompanied by a reduction, the oxidizing agent being itself reduced in the operation. As seen in the above equations, the manganic compound is reduced to a manganous compound, and the chromic to a chromous compound.

#### ESTIMATION OF FERROUS SALTS.

Ferrous salts are estimated by oxidizing them either with potassium dichromate or potassium permanganate.

In some respects the dichromate possesses advantages over permanganate.

1. It may be obtained in a pure state.
2. Its solution does not deteriorate upon standing as does that of permanganate.
3. It is not decomposed by contact with rubber as the permanganate is, and may therefore be used in Mohr's burette. Its great disadvantage, however, is that when used in the estimation of ferrous salts the end reaction can only be found by using an external indicator. The indicator which must be used is freshly

prepared potassium ferricyanide T. S., a drop of which is brought in contact with a drop of the solution being tested, on a white slab, at intervals during the titration, the end of the reaction being the cessation of the production of a blue color, when the two liquids are brought together. Thus the estimation by potassium dichromate is cumbersome, and very exact results are not easily obtained.

If potassium-permanganate solution is used for the estimation of these salts the end of the reaction is easily found without the use of an indicator.

The permanganate is decomposed the instant it is brought in contact with a ferrous salt in an acid solution; therefore as long as any ferrous salt remains in solution the permanganate is decolorized, and when it ceases to lose its color the reaction is complete.

### Preparation of Standard Solution Decinormal

**Potassium Dichromate V. S.**,  $K_2Cr_2O_7 = \left\{ \begin{array}{l} 293.78 \\ *294 \end{array} \right.$

$\left. \begin{array}{l} 4.896 \\ *4.9 \end{array} \right\}$  gms. in 1 litre.—4.896 gms. (\*4.9 gms.) of pure potassium dichromate are dissolved in sufficient water to make, at the ordinary temperature of the atmosphere, exactly 1000 cc.

*Pure Potassium Dichromate* for use in volumetric analysis should respond to all the tests for purity given in the text of the U. S. P. (under *Potassii Dichromate*), as well as to the following: A solution of 0.5 gm. of the salt in 10 cc. of water, rendered acid by 0.5 cc. of nitric acid, should produce no visible change when treated with barium chloride T. S. (absence of *sulphate*), nor with silver nitrate T. S. (absence of *chloride*).

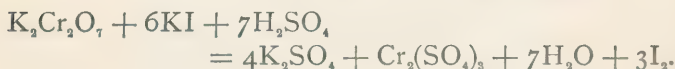
If a mixture of 10 cc. of an aqueous solution of the

salt (1-20) with 1 cc. of ammonia water be treated with ammonium oxalate T. S., no precipitate should be produced (absence of *calcium*).

Standard solution of potassium dichromate is sometimes used as a neutralizing solution for estimating alkalis, phenolphthalein being used as indicator.

When used for this purpose the decinormal solution contains 14.689 gms. in 1 litre (one half the molecular weight in grammes). It is then the exact equivalent of any decinormal acid V. S.

Decinormal potassium dichromate V. S. may also be used in conjunction with potassium iodide and sulphuric acid for standardizing sodium thiosulphate V. S. Iodine is liberated from potassium iodide in this reaction. The reaction is expressed by the equation



When used as an oxidizing agent to convert ferrous into ferric salts, or to liberate iodine from potassium iodide, the  $\frac{\text{N}}{10}$  solution of potassium dichromate must contain 4.689 gms. in 1 litre. If the decinormal solution containing 14.689 gms. in 1 litre is used, it has the effect of a  $\frac{3\text{N}}{10}$  solution.

The decinormal solution which is used as an oxidizing agent is chemically equivalent to decinormal potassium permanganate. When used for the purpose of liberating iodine from potassium iodide, it is the equivalent of an equal volume of decinormal sodium thiosulphate.

*For titrating ferrous salts* the decinormal solution of dichromate is used in the following manner:

Make an aqueous solution of the ferrous salt, introduce it into a flask, and acidulate it with sulphuric or hydrochloric acid. Now add gradually from a burette the decinormal potassium dichromate V. S. until a drop taken out upon a white slab no longer shows a blue color with a drop of freshly prepared potassium ferricyanide T. S. Note the number of cc. of the standard solution used, multiply this number by the factor, and thus obtain the quantity of pure salt in the sample taken.

Ferrous salts strike a blue color with potassium ferricyanide T. S; but as the quantity of ferrous salts gradually diminishes during the titration, the blue becomes somewhat turbid, acquiring first a green, then a gray, and lastly a brown shade. The process is finished when the greenish-blue tint has entirely disappeared.

The reaction of potassium dichromate with ferrous salts always takes place in the presence of free sulphuric or hydrochloric acid at ordinary temperatures. Nitric acid should not be used.

If it is desired to estimate ferric salts by this standard solution it is necessary to first reduce them.

This may be done by metallic zinc, magnesium, sulphurous acid, the alkali sulphites, or by stannous chloride.

Standard potassium dichromate may be checked in the same way as standard permanganate, with pure metallic iron, as described below.

#### Decinormal Potassium Permanganate V. S.,

$2\text{KMnO}_4 = \left\{ \begin{array}{l} 315.34 \\ *316 \end{array} \right.$ . It contains  $\left\{ \begin{array}{l} 3.1534 \\ *3.16 \end{array} \right.$  } gms. in 1

litre.—This solution may be prepared by dissolving the pure crystals in fresh distilled water. If the salt can be

obtained perfectly pure and dry, a decinormal solution will be obtained if 3.1534 gms. are dissolved in distilled water, sufficient to make 1000 cc. at the ordinary atmospheric temperature; but nevertheless it is always well to verify it as described below. The solution will retain its strength for several weeks if well kept, but it should always be checked by titration before it is used.

The standardization of permanganate solution may be effected as follows:

*With Metallic Iron*—Thin annealed binding-wire, free from rust, is one of the purest forms of iron.

0.1 gm. of such iron is placed in a flask which is



FIG. 24.

provided with a cork through which a piece of glass tubing passes, to the top of which a piece of rubber tubing is attached, which has a vertical slit about one inch long in its side, and which is closed at its upper end by a piece of glass rod (see Fig. 24). Diluted sulphuric acid is added and gentle heat applied. The iron dissolves and the steam and liberated hydrogen escape through the slit under slight pressure. The air is thus prevented from entering and the ferrous solution

protected from oxidation.

When the iron is completely dissolved a small quantity of cold, recently boiled, distilled water should be added, and the titration with potassium permanganate at once begun and continued until a faint permanent

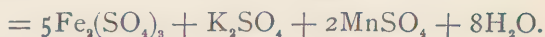


red color is produced. If the solution is decinormal, exactly 17.85 cc. will be required to produce this result.

The iron is converted by the sulphuric acid into ferrous sulphate,  $\text{Fe}_2 + 2\text{H}_2\text{SO}_4 = 2\text{FeSO}_4 + 2\text{H}_2$ . This ferrous sulphate is easily oxidized by the air, and therefore it is directed that access of air should be prevented, and the distilled water, with which the solution is diluted, previously boiled in order to drive off any dissolved free oxygen.

$$10\text{FeSO}_4 + 2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4$$

100)558.8	100)315.34	
5.588 gms.	3.1534 gms.	or 1000 cc. $\frac{N}{10}$ V. S.



This equation, etc., shows that each cc. of  $\frac{N}{10}$   $2\text{KMnO}_4$  V. S. represents .005588 gm. of metallic iron.

*With Oxalic Acid.*—0.063 gm. of the pure crystallized acid is weighed (or 10 cc. of decinormal oxalic acid V. S. carefully measured) and placed in a flask, with some dilute sulphuric acid and considerable water, the mixture warmed to about 60° C. (140° F.), and the permanganate added from a burette.

The action is in this case less decisive and rapid than in the titration with iron, and more care should be used. The color disappears slowly at first, but afterwards more rapidly.

Note the number of cc. of the permanganate solution used, and then dilute the remainder so that equal volumes of decinormal oxalic acid and decinormal permanganate solution will exactly correspond.



*Example.*—Assuming that 9 cc. of the permanganate solution first prepared had been required to produce a permanent pink tint when titrated into 10 cc. of  $\frac{N}{10}$  oxalic-acid solution, then the permanganate must be diluted in the proportion of 9 of permanganate and 1 of distilled water, or 900 and 100.

The U. S. P. gives the following method for the preparation of this solution :

A stronger and a weaker solution is made and mixed in certain proportions to form a solution of the proper strength. It is said that when thus prepared the solution will keep its titre for months if properly preserved.

*The Stronger Solution.*—3.5 gms. of pure crystallized permanganate are dissolved in 1000 cc. of water by the aid of heat, and the solution then set aside in a closed flask for two days, so that any suspended matters may deposit.

*The Weaker Solution.*—Dissolve 6.6 gms. of the salt in 2200 cc. of water in the same manner as above, and set this solution aside for two days.

These two solutions are then separately titrated in the following manner :

Introduce 10 cc. of decinormal oxalic-acid solution into a flask, add 1 cc. of pure concentrated sulphuric acid, and before the mixture cools add the permanganate solution slowly from a burette, shaking the flask after each addition, and towards the end of the operation reducing the flow to drops. When the last drop is no longer decolorized, but imparts a pinkish tint to the liquid, the reaction is completed. Note the number of cc. consumed. Finally, mix the two solutions in such proportions that equal volumes of the

mixture and of  $\frac{N}{10}$  oxalic acid V. S. will exactly correspond.

To obtain the accurate proportions for mixing the two solutions, deduct 10 from the number of cc. of the weaker solution consumed in the above titration; with this difference multiply the number of cc. of the stronger solution consumed: the product shows the number of cc. of the *stronger solution* needed for the mixture.

Then deduct the number of cc. of the stronger solution consumed in the titration from 10, and with the difference multiply the number of cc. of the weaker solution consumed: the product shows the number of cc. of the *weaker solution* needed for the mixture.

Or, designating the number of cc. of the stronger solution by  $S$ , and the number of cc. of the weaker solution by  $W$ , and using the following formula, the proportions in which the solutions must be mixed are obtained:

$$\begin{array}{rcl} \text{Stronger Solution.} & & \text{Weaker Solution.} \\ (W - 10)S & + & (10 - S)W. \end{array}$$

*Example.*—Assuming that 9 cc. of the stronger and 10.5 cc. of weaker had been consumed in decomposing 10 cc. of  $\frac{N}{10}$  oxalic acid V. S.; then, substituting these values in the above formula, we obtain

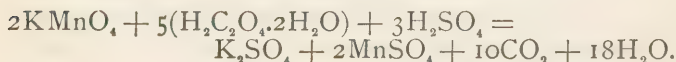
$$\begin{array}{rcl} (10.5 - 10)9 & + & (10 - 9)10.5, \\ \text{or } 4.5 & + & 10.5, \end{array}$$

making 15 cc. of final solution.

The bulk of the two solutions is now mixed in the same proportion : 450 cc. of the stronger and 1050 cc. of the weaker, or 900 cc. of the stronger and 2100 cc. of the weaker.

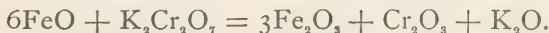
After the solutions are thus mixed a new trial should be made, when 10 cc. of the solution should exactly decompose 10 cc. of  $\frac{N}{10}$  oxalic acid V. S.

The reaction between potassium permanganate and oxalic acid is illustrated by the following equation :



#### ESTIMATION OF FERROUS SALTS WITH POTASSIUM DICHROMATE.

One molecule of potassium dichromate yields, under favorable circumstances, three atoms of oxygen for oxidizing purposes. This is shown by the following equation :



Here it is seen that the three liberated atoms of oxygen combine at once with the ferrous oxide, converting it into ferric oxide :

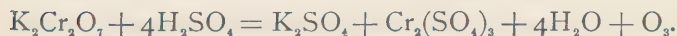


When used for oxidizing, the reaction takes place only in the presence of an acid.

The dichromate then gives up its oxygen. Four of

its oxygen atoms combine at once with the replaceable hydrogen of the accompanying acid, the other three being liberated. The three oxygen atoms thus set free are available either for direct oxidation or for combination with the hydrogen of more acid. In the latter case a corresponding quantity of acidulous radicals is set free.

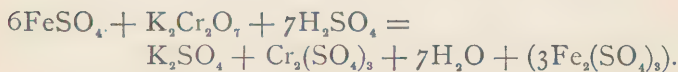
The following equation indicates this reaction :



In this case four of the liberated atoms of oxygen combine with eight of the atoms of hydrogen of sulphuric acid and liberate four  $\text{SO}_4$  radicals, which at once combine with the  $\text{K}_2$  and  $\text{Cr}_2$  of the dichromate. The other three atoms are set free. If seven sulphuric-acid molecules are used instead of four molecules, the three free atoms of oxygen will liberate  $3(\text{SO}_4)$ :



If this liberation of  $3(\text{SO}_4)$  takes place in the presence of a ferrous salt, the  $3(\text{SO}_4)$  will combine with six molecules of the ferrous salt, converting it into a ferric salt :



If in the above case hydrochloric acid is used instead of sulphuric, fourteen molecules of the former must be taken to supply the necessary hydrogen.

The seven liberated atoms of oxygen must have fourteen atoms of hydrogen to combine with.

Three of these atoms of oxygen liberate six univalent, or three bivalent, acidulous radicals.

Therefore, since one molecule of  $K_2Cr_2O_7$  will give up for oxidizing purposes three atoms of oxygen, which are equivalent chemically to six atoms of hydrogen, one sixth of the molecular weight in grammes of the dichromate, dissolved in sufficient water to make one litre, constitutes a normal solution, and one tenth of this quantity of  $K_2Cr_2O_7$  in a litre, a decinormal solution.

Thus the estimation of ferrous salts is effected by oxidizing them to ferric with an oxidizing agent of known power, the strength of the ferrous salt being determined by the quantity of the oxidizing agent required to convert it to ferric.

**Ferri Carbonas Saccharatus** (Saccharated Ferrous Carbonate),  $FeCO_3 = \left\{ \begin{array}{l} 115.73 \\ *116 \end{array} \right.$  —  $*1.16$  (1.1573) gms. of saccharated ferrous carbonate are dissolved in 10 cc. of diluted sulphuric acid and the solution diluted with water to about 100 cc. The decinormal potassium dichromate is carefully added, until a drop of the solution taken out and brought in contact with a drop of freshly prepared solution of potassium ferricyanide ceases to give a blue color.

The number of cc. of the dichromate solution is read off and the following equations applied :



$$\begin{array}{r} 115.73 \\ 6 \\ \hline 694.38 \end{array}$$

$$\begin{array}{r} 151.7 \\ 6 \\ \hline 910.2 \end{array}$$

then

$$\begin{array}{r}
 6\text{FeCO}_3 \text{ or } 6\text{FeSO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{SO}_4 = \\
 \begin{array}{r}
 6)694.38 \\
 10)115.73 \\
 \hline
 11.573 \text{ gms.}
 \end{array}
 \begin{array}{r}
 6)910.2 \\
 10)151.7 \\
 \hline
 15.17 \text{ gms.}
 \end{array}
 \begin{array}{r}
 6)293.78 \\
 10)48.96 \\
 \hline
 4.896 \text{ gms., or } 1000 \text{ cc. } \frac{\text{N}}{10} \text{ K}_2\text{Cr}_2\text{O}_7 \text{ V.S.}
 \end{array}
 \end{array}$$



Thus each cc. of  $\frac{\text{N}}{10} \text{K}_2\text{Cr}_2\text{O}_7$  represents 0.011573 gm. of pure ferrous carbonate or 0.005588 gm. of metallic iron.

The U. S. P. saccharated ferrous carbonate requires about 15 cc. of  $\frac{\text{N}}{10} \text{K}_2\text{Cr}_2\text{O}_7$  V. S. for complete neutralization, corresponding to about 15%.

$$\begin{aligned}
 0.011573 \times 15 &= 0.173585 \text{ gm.} \\
 \frac{0.173585 \times 100}{1.1573} &= 15\%
 \end{aligned}$$

If strong sulphuric acid is added to saccharated ferrous carbonate it will char the sugar, and a black mass of burnt sugar is obtained. This may be prevented by adding water first and then, slowly, the sulphuric acid.

Instead of sulphuric acid, hydrochloric acid may be used. This will not char the sugar; but the ferrous chloride which is then formed is too readily oxidized by the air.

It has also been suggested that as hydrochloric acid so rapidly converts ordinary sugar into invert sugar as to render it easily attacked by the dichromate, it should be cautiously used, if at all. Phosphoric acid

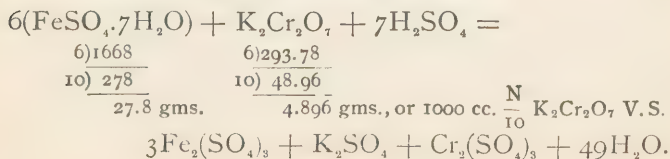
has none of these disadvantages, and may be employed with good results.

In making estimations of ferrous salts with potassium dichromate, care should be taken to avoid atmospheric oxidation. It is good practice to calculate approximately how much of the standard solution will probably be required to complete the oxidation, and then add almost enough of the standard solution at once, instead of adding it slowly.

A white porcelain slab is then got ready, and placed alongside of the flask in which the titration is to be performed. Upon this slab is placed a number of drops of the freshly prepared solution of potassium ferricyanide, and at intervals during the titration a drop is taken from the flask on a glass rod and brought in contact with one of the drops on the slab. The glass rod should always be dipped in clean water after having been brought in contact with a drop of the indicator.

When a drop of the solution ceases to give a blue color on contact with the indicator, the reaction is complete.

**Ferrous Sulphate,**  $\text{FeSO}_4 + 7\text{H}_2\text{O} = \left\{ \begin{array}{l} 277.42 \\ *278 \end{array} \right.$ .—Dissolve about one gramme of crystallized ferrous sulphate in a little water, add a good excess of sulphuric or hydrochloric acid, titrate with the decinormal potassium dichromate V. S. as directed under Ferrous Carbonate, and apply the following equation:





Thus each cc. of the  $\frac{N}{10}$   $K_2Cr_2O_7$  V. S. represents 0.0278 gm. of crystallized ferrous sulphate or 0.0152 anhydrous. If 1 gm. of the salt is taken and dissolved as above, it should require about 37 cc. of the standard solution, equivalent to about 100%.

*Anhydrous Ferrous Sulphate.*—



$$\begin{array}{r} 6)912 \\ 10)152 \\ \hline 15.2 \text{ gms.} \end{array} \quad \begin{array}{r} 6)293.78 \\ 10)48.96 \\ \hline 4.896 \text{ gms., or } 1000 \text{ cc.} \end{array} \quad \frac{N}{10} K_2Cr_2O_7 \text{ V. S.}$$



Each cc. of the standard solution represents 0.0152 gm. of real ferrous sulphate or \*.0056 gm. of metallic iron.

*Dried (Exsiccated) Ferrous Sulphate* of the U. S. P. has the approximate composition  $FeSO_4 + 3H_2O$ .

It is tested in the same manner as the anhydrous ferrous sulphate.

*Granulated Ferrous Sulphate*,  $FeSO_4 + 7H_2O$ , is tested in the same manner as crystallized ferrous sulphate, with which it should correspond in strength.

#### ESTIMATION OF FERROUS SALTS WITH POTASSIUM-PERMANGANATE SOLUTION.

The action of potassium permanganate in oxidation is very similar to that of the dichromate.

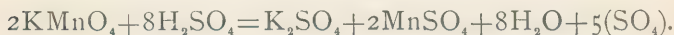
The molecule  $2KMnO_4$  has 8 atoms of oxygen, which it gives up in the process of oxidation. These 8 atoms of oxygen unite with the replaceable hydrogen

of an accompanying acid, liberating an equivalent amount of acidulous radical.

Three of these atoms of oxygen liberate sufficient acidulous radical to combine with the potassium and manganese of the permanganate, while the other five atoms are available either for direct oxidation or



For combination with the hydrogen of more acid, more acidulous radical being liberated to combine with the salt acted upon,



$5(\text{SO}_4)$  when combined with  $10\text{FeSO}_4$  forms  $\text{Fe}_{10}(\text{SO}_4)_{15}$  or  $5\text{Fe}_2(\text{SO}_4)_3$ , ferric sulphate.

It is thus seen that one molecule of potassium permanganate  $2\text{KMnO}_4$  has the power of converting 10 molecules of a ferrous salt into the ferric state.

The equation in full is



We have seen that  $2\text{KMnO}_4$  has 5 atoms of oxygen available for oxidizing purposes, and that each of these will combine with 2 atoms of hydrogen.  $2\text{KMnO}_4$  is consequently chemically equivalent to 10 atoms of replaceable hydrogen, and a normal solution of this salt when used as an oxidizing agent is one that contains in 1 litre one tenth of the molecular weight of  $2\text{KMnO}_4$ , and a decinormal solution one which contains one hundredth of the molecular weight,

When potassium permanganate is brought in contact with a ferrous salt or other oxidizable substance, it is decomposed and decolorized.

When titrating with a standard solution of this salt it is decolorized so long as an oxidizable substance is present; as soon, however, as the oxidation is completed the standard solution retains its color.

The end of the reaction, therefore, when permanganate is used, is the appearance of a permanent faint-red color.

This is the principal advantage which permanganate has over dichromate.

When titrating with standard permanganate solution a glass stop-cock burette should be used, as the solution is slightly affected by the rubber on Mohr's burette.

**Ferrum Reductum** is estimated for metallic iron, according to the U. S. P., in the following manner:

0.56 (0.559) gm. of reduced iron is introduced into a glass-stoppered bottle, 50 cc. of *mercuric chloride* T. S. are added, and the bottle heated on a water-bath for one hour, agitating frequently, but keeping the bottle well stoppered.

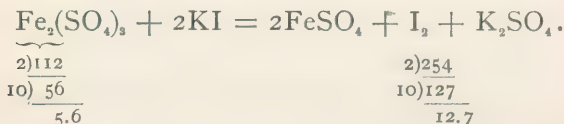


Then allow it to cool, dilute the contents with water to 100 cc., and filter. Take 10 cc. of the filtrate, add to it 10 cc. of diluted sulphuric acid, introduce the mixture into a glass-stoppered bottle (having a capacity of about 100 cc.), and titrate the mixture with decinormal potassium permanganate V. S. until a permanent red color is produced.

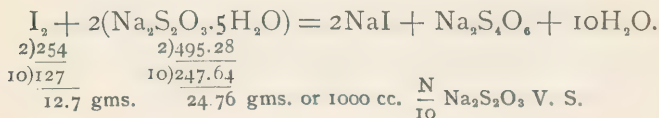
Each cc. of the standard solution represents \*0.0056 gm. of metallic iron, or 10%.



To confirm the assay, add a few drops of alcohol to decolorize (or decompose) the excess of permanganate, then add 1 gm. of potassium iodide, and digest for half an hour at a temperature of 40° C. (104° F.).



The cooled solution is mixed with a few drops of starch test solution, which gives it a dark-blue color, because of the formation of iodide of starch. Then add carefully, from a burette, decinormal sodium thiosulphate V. S. until the blue color is discharged.



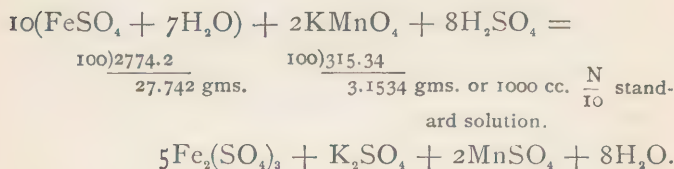
Thus each cc. of the standard thiosulphate represents 0.0127 gm. of iodine, or 0.0056 gm. of metallic iron.

In both of these estimations the quantity of standard solution used should be the same.

The U. S. P. requirement is 8 cc.

$$\begin{aligned} 0.0056 \times 8 &= 0.0448 \text{ gm.} \\ \frac{0.0448 \times 100}{0.056} &= 80\% \end{aligned}$$

**Ferrous Sulphate** (Crystallized),  $\text{FeSO}_4 + 7\text{H}_2\text{O} =$   
 $\left\{ \begin{array}{l} 277.42 \\ *278 \end{array} \right. \cdot *1.39 \text{ (1.3871) gms. of ferrous sulphate are}$   
 dissolved in about 25 cc. of water, and the solution acidulated with sulphuric acid. Decinormal potassium permanganate V. S. is then delivered in from a burette until a permanent pink color is obtained, indicating the complete oxidation of the ferrous salt.



Thus each cc. of the standard solution represents 0.027742 gm. of crystallized ferrous sulphate.

Not less than 50 cc. should be used before the potassium permanganate ceases to be decolorized.

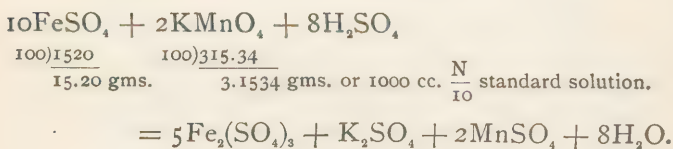
$$\begin{aligned} 0.027742 \times 50 &= 1.387100 \text{ gms.} \\ \frac{1.387100 \times 100}{1.3871} &= 100\% \end{aligned}$$

*Granulated Ferrous Sulphate*,  $\text{FeSO}_4 + 7\text{H}_2\text{O}$ , is estimated in the same way as the foregoing, and should correspond with it in strength.

*Exsiccated (Dried) Ferrous Sulphate*.—This salt is tested in the same manner as the other two sulphates. It contains a larger percentage of ferrous sulphate than the other two, having less water of crystallization. Its composition is approximately  $\text{FeSO}_4 + 3\text{H}_2\text{O}$ .

In estimating ferrous sulphate in this salt the water of crystallization is not taken into account. Then by

deducting the percentage of ferrous sulphate from 100 the percentage of water of crystallization is obtained.



Each cc. of the standard solution represents 0.0152 gm. of anhydrous (real) ferrous sulphate. If one gm. of the dried salt, treated as above described, requires

48 cc. of  $\frac{\text{N}}{10}$  permanganate solution, it contains

$$0.0152 \times 48 = 0.7296 \text{ gm.,}$$

or 72.96% of real ferrous sulphate, and  $100.00 - 72.96 = 27.04\%$  of water of crystallization.

Any salt may be analyzed in this way for water of crystallization. If the salt is *pure*, the difference between the percentage of real salt and 100 always represents the percentage of water of crystallization.

#### ESTIMATION OF HYPOPHOSPHOROUS ACID, HYPOPHOSPHITES, AND OTHER OXIDIZABLE SUBSTANCES.

**Acidum Hypophosphorosum Dilutum.**—An aqueous solution containing about 10 per cent, by weight, of absolute hypophosphorous acid.

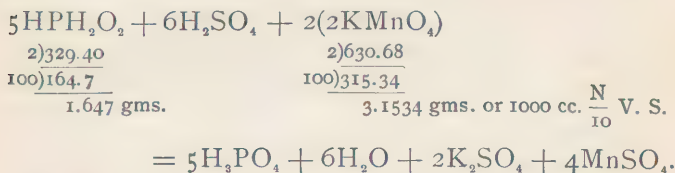


This acid may be tested by neutralization with  $\frac{\text{N}}{1}$  potassium hydrate V. S., as described in Chapter X.

The U. S. P. also directs the estimation by residual titration, given below.

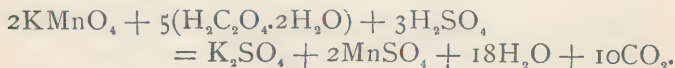
0.5 gm. of diluted hypophosphorous acid is mixed with 7 cc. of sulphuric acid, and 35 cc. of decinormal potassium permanganate V. S., and the mixture boiled for fifteen minutes.

The potassium permanganate, in the presence of sulphuric acid, oxidizes the hypophosphorous acid to phosphoric, as the equation shows:



Each cc. of the decinormal V. S. represents 0.001647 gm. of absolute hypophosphorous acid. The quantity of permanganate solution directed to be added is slightly in excess. The excess is then ascertained by retitration with decinormal oxalic acid V. S. Each cc. of oxalic acid required corresponds to one cc. of decinormal permanganate V. S., which has been added in excess of the quantity actually required for the oxidation.

The excess of permanganate colors the solution red, and the oxalic acid V. S. is then added until the red color just disappears, which indicates that the excess of permanganate is decomposed.



If 4.7 cc. of decinormal oxalic acid V. S. are required, it indicates that 35 cc. - 4.7 cc. = 30.3 cc. of deci-



normal permanganate were actually used up in oxidizing the hypophosphorous acid.

Therefore

$$0.001647 \text{ gm.} \times 30.3 = 0.0499 \text{ gm.,}$$

$$\text{or } \frac{0.0499 \times 100}{.5} = 9.98\% \text{ of } \text{HPH}_2\text{O}_2.$$

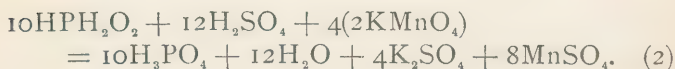
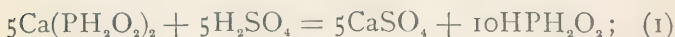
In the above process the boiling facilitates the oxidation, but if the acid is boiled before it is completely oxidized it will decompose. Hence the necessity for adding an excess of the permanganate and retitrating.

**Calcium Hypophosphite**,  $\text{Ca}(\text{PH}_2\text{O}_2)_2 = \left\{ \begin{array}{l} 169.67 \\ *170 \end{array} \right.$

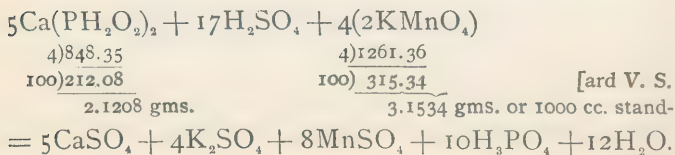
—0.1 gm. of the salt is dissolved in 10 cc. of water, then 10 cc. of sulphuric acid and 50 cc. of decinormal potassium permanganate V. S. are added, and the mixture boiled for fifteen minutes.

The excess of permanganate is then found by retitrating with decinormal oxalic-acid solution.

The reactions which take place are expressed by the following equations:



These two reactions may be written together thus:



Thus each cc. of the standard permanganate represents 0.0021208 gm. of pure  $\text{Ca}(\text{PH}_2\text{O}_2)_2$ . 50 cc. of decinormal potassium permanganate are about 3 cc. more than is necessary to oxidize 0.1 gm. of pure calcium hypophosphite. Therefore not more than 3 cc. of the standard oxalic-acid solution should be required to decolorize the solution to which 50 cc. of permanganate has been added.

Then

$$0.0021208 \text{ gm.} \times 47 = .09968 \text{ gm.}$$

$$\frac{0.9968 \times 100}{0.1} = 99.68\% \text{ pure salt.}$$

**Ferric Hypophosphite**,  $\text{Fe}_2(\text{PH}_2\text{O}_2)_6 = \left\{ \begin{array}{l} 501.04. \\ *501 \end{array} \right.$

—This salt is estimated in the same manner as the foregoing.

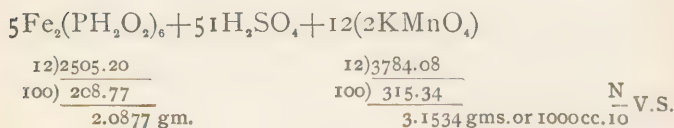
0.1 gm. is dissolved in 10 cc. of water, then 10 cc. of sulphuric acid and 50 cc. of decinormal potassium permanganate V. S. are added, and the mixture boiled for 15 minutes.

The quantity of permanganate solution here added is slightly in excess of the quantity actually required to oxidize the hypophosphite. The excess is determined by retitrating with decinormal oxalic acid V. S., which corresponds volume for volume with the permanganate.

Not more than 3 cc. of the standard oxalic acid solution should be required to decolorize the excess of permanganate, which means that 47 c.c. of the per-

manganate should actually be required to oxidize the 0.1 gm. of hypophosphite taken.

The reaction is illustrated by the following equation :

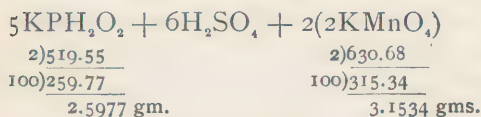


This shows that each cc. of  $\frac{\text{N}}{10}$  potassium permanganate V. S. represents 0.0020877 gm. of ferric hypophosphite. If 47 cc. are required to oxidize 0.1 gm. of the salt, the latter contains  $0.0020877 \times 47 = 0.0981+$  gm., or 98.1+ % of pure salt.

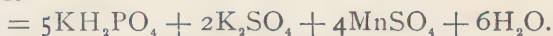
**Potassium Hypophosphite**,  $\text{KPH}_2\text{O}_2 = \left\{ \begin{array}{l} 103.91 \\ *104 \end{array} \right.$ .  
 —0.1 gm. of dry potassium hypophosphite is dissolved in about 10 cc. of water, then 7.5 cc. of sulphuric acid and 40 cc. of decinormal potassium permanganate V. S. are added, and the mixture is boiled for 15 minutes.

Decinormal oxalic acid is then carefully delivered into the mixture until the red color, due to the excess of permanganate, is discharged. The number of cc. of the standard oxalic acid required for this purpose, subtracted from the 40 cc. of permanganate originally added, gives the quantity of permanganate which was actually required for the oxidation of the hypophosphite. If the salt conforms in purity to the U. S. P. requirement, not more than 2 cc. of the oxalic acid V. S. will be required.

The following equation illustrates the reaction which takes place in this operation :



or 1000 cc.  $\frac{\text{N}}{10}$  permanganate V. S.

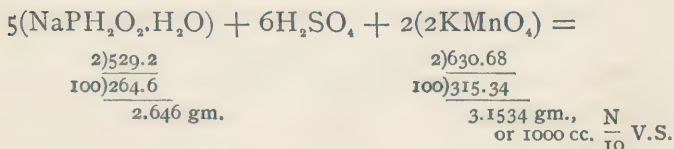


Each cc. of decinormal permanganate V. S. required for the oxidation of the hypophosphite, represents 0.0025977 gm. of the pure salt. If 38 cc. are required, then  $0.0025977 \times 38 = .0987126$  gm., or 98.7+ %.

**Sodium Hypophosphite**,  $\text{NaPH}_2\text{O}_2 + \text{H}_2\text{O} =$   
 $\left\{ \begin{array}{l} 105.84. \\ *106 \end{array} \right.$ —0.1 gm. of the dry salt is dissolved in 10 cc. of water and mixed with 7.5 cc. sulphuric acid and 40 cc. of decinormal potassium permanganate V. S. The mixture is then boiled for 15 minutes, and titrated with decinormal oxalic-acid solution to determine the excess of permanganate.

Not more than 3 cc. of the oxalic acid V. S. should be required to discharge the red color, which means that 0.1 gm. of the salt should require 37 cc. of  $\frac{\text{N}}{10}$  permanganate solution for its oxidation.

The following equation shows the reaction :



Thus each cc. of the decinormal permanganate represents 0.002646 gm. of  $\text{NaPH}_2\text{O}_2$ .

Therefore  $0.002646 \times 37 = 0.097902$  gm. or 97.9%.

**Aqua Hydrogenii Dioxidii U. S. P.** (Solution of Hydrogen Peroxide).—It is described in the U. S. P. as an aqueous solution of hydrogen dioxide,  $\text{H}_2\text{O}_2 =$   
 $\left\{ \begin{array}{l} 33.9^2 \\ *34 \end{array} \right.$ , slightly acid and containing about 3%, by weight, of pure dioxide, corresponding to 10 volumes of available oxygen.

This substance is official for the first time in the U. S. P. 1890, in which methods for its preparation, preservation, and assay are given. Solution of hydrogen peroxide is an important commercial product, being used in the arts as well as in medicine.

It is sold as containing 5, 10, 15, or 20 volumes of oxygen, in solution. This should mean that a given volume of the solution yields from itself 5, 10, 15, or 20 times its own volume of oxygen.

Thus, 1 cc. of a 5-volume solution yields 5 cc. of oxygen; a 10-volume solution is one of which 1 cc. will yield 10 cc. of oxygen; etc.

Many solutions of hydrogen dioxide are sent into the market under false pretences, being labelled as containing 10, 15, or 20 volumes of oxygen.

It is true a given volume of these solutions will yield the specified volume of oxygen when decomposed with potassium permanganate, but half of this oxygen comes from the permanganate itself. Therefore the peroxide of hydrogen solution contains only half as much available oxygen as is given off in this decomposition.

Freshly bought samples of the five largest manufac-

turers, according to the analyses of Dr. Edward R. Squibb (*Ephemeris*, vol. IV. No. 2), gave 9.2, 8.7, 8.4, 10.9, 9.7, 8.6, 8.5, 7.3, and 7.4 volumes. All of these were labelled as being of 15 volumes strength. The author has had a similar experience.

In its purest and most concentrated form peroxide of hydrogen is a syrupy colorless liquid, having an odor resembling that of chlorine or ozone.

One cc. of this concentrated hydrogen peroxide when decomposed at 0° C. evolves 330.3 times its own volume of oxygen, at a pressure of 760 mm. at 45° N. latitude.

At a temperature of 100° C. (212° F.)  $H_2O_2$  decomposes rapidly into water and oxygen. This change also takes place at ordinary temperatures, but more slowly. In diluted solutions it is more stable, and may be concentrated by boiling without suffering much decomposition.

Dr. Squibb made a series of experiments in order to prove this, as well as the fact that solutions of hydrogen peroxide when kept in open vessels at the ordinary temperature become stronger, instead of weaker as was generally supposed. The water evaporates more rapidly than the peroxide decomposes. Part of the results of these experiments as published in the *Ephemeris*, vol. IV. No. 2, is as follows:

A freshly made solution that yielded 10.3 volumes of available oxygen was taken as the basis of the experiment. The evaporation was done on a water-bath, at temperatures varying from 55° to 62° C. (131° to 143.6° F.); one cc. of the concentrated solution being taken out for testing after each evaporation.

200 cc. evaporated in 2 hours to 100 cc. tested 20.6 volumes: no apparent loss.



100 cc. of the 10.3-volume solution were added, and evaporated in 2 hours to 100 cc., tested 29.6 volumes: 1.3 volumes loss.

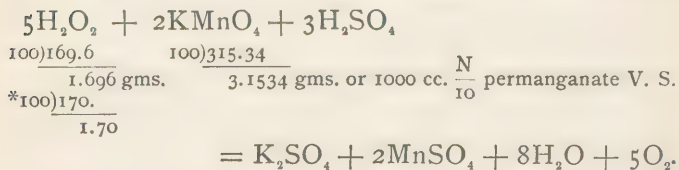
100 cc. of the 10.3-volume solution were added, and evaporated in 2 hours to 100 cc., tested 36.5 volumes: 4.7 volumes loss.

100 cc. of the 10.3-volume solution were added, and evaporated in 2.5 hours to 23 cc., tested 146.8 volumes.

Another series of evaporations were made at higher temperatures, which also showed an increase in strength, but the loss was a little larger.

**The Assay of Hydrogen Peroxide,  $H_2O_2$**   
 $= \left\{ \begin{array}{l} 33.92 \\ *34 \end{array} \right.$ .—The U. S. P. method is as follows:  
 10 cc. of the solution are diluted with water to make 100 cc. Transfer 17 cc. of this liquid (containing 1.7 cc. of the solution of  $H_2O_2$ ) to a beaker, add 5 cc. of diluted sulphuric acid, and then from a burette  $\frac{N}{10}$  potassium permanganate V. S. until the liquid just retains a faint-pink tint after being stirred.

The reaction is expressed by the following equation:



Thus each cc. of the  $\frac{N}{10}$  potassium permanganate represents .001696 (\*.0017) gm. of absolute hydrogen dioxide.



The U. S. P. requires that 1.7 gms. of the solution of peroxide should decolorize 30 cc. of  $\frac{N}{10}$  permanganate solution.

This corresponds to 3 per cent. by weight, of  $H_2O_2$ .

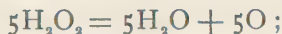
$$.0017 \times 30 = .051 \text{ gm.}$$

$$\frac{.051 \times 100}{1.7} = 3\%$$

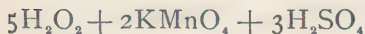
**Estimation of Volume Strength.**—Let us look at the above equation in a different light.

We there see that when potassium permanganate and hydrogen peroxide react, 10 atoms of oxygen are liberated.

The permanganate itself when decomposed liberates five atoms of oxygen. Therefore of the above ten atoms only five come from the peroxide of hydrogen.



In order to find the factor for volume of available oxygen, see the following equation, etc.:



$$\begin{array}{r} 100 \overline{) 315.34} \end{array}$$

3.1534 gms. or 1000 cc. of  $\frac{N}{10}$  V. S.



$$\begin{array}{r} 100 \overline{) 79.8} \end{array}$$

.798 gm.

$$\begin{array}{r} 100 \overline{) 80} \end{array}$$

\*.80 gm.

Thus it is seen that each cc. of  $\frac{N}{10}$  potassium permanganate represents .000798 (\*.0008) gm. of oxygen.

But we wish to find the volume of oxygen, not the weight represented by 1 cc. of the  $\frac{N}{10}$  permanganate. 1000 cc. of oxygen at 0° C. and 760 mm. pressure weigh 1.424488 grammes, \*(1.43 gms.).

Therefore, if 1.43 gms. measure 1000 cc., .0008 gm. will measure  $x$ .

$$x = 0.5594 \text{ cc.}$$

$$\frac{1000 \times .0008}{1.43} = 0.5594 \text{ cc.}$$

The factor, then, for volume of oxygen, liberated when peroxide of hydrogen is titrated with  $\frac{N}{10}$  potassium permanganate is 0.5594, and the number of cc. of the  $\frac{N}{10}$  potassium permanganate consumed in the titration gives the volume of oxygen liberated by the quantity of hydrogen peroxide taken.

Thus if 30 cc. of the  $\frac{N}{10}$  V. S. were required,

$$0.5594 \times 30 = 16.782 \text{ cc. of oxygen,}$$

$$\begin{array}{r} 1.7 \overline{)16.782} \\ 9.87 \text{ volume strength.} \end{array}$$

or the number of cc. of oxygen liberated by 1 cc. of the peroxide solution tested.

It is convenient to operate upon 1 cc. hydrogen-peroxide solution. Then each cc. of potassium per-

manganate V. S. used will represent 0.5594 cc. of available oxygen, or 0.0008 gm. of oxygen, and it is only necessary to multiply the cc. by these numbers to obtain the volume or weight of available oxygen.

Hydrogen-peroxide solution may also be volumetrically assayed by Kingzett's method, which is described in the chapter on Iodimetry.

The gasometric estimation is also described further on.

**Barium Dioxide** (Barium Peroxide),  $\text{BaO}_2 = \begin{cases} 168.82 \\ *168.9 \end{cases}$ .—This substance is assayed by treating it with an acid, and then estimating the liberated hydrogen dioxide, as follows:

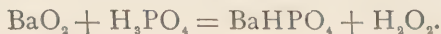
Weigh off 2.11 gms. of the coarse powder, put it in a porcelain capsule, add about 10 cc. of ice-cold water, then 7.5 cc. of phosphoric acid, U. S. P., and sufficient ice-cold water to make 25 cc. Stir and break up the particles with the end of the stirrer until a clear or nearly clear solution is obtained, and all that is soluble is dissolved.

5 cc. of this solution (which corresponds to 0.422 gm. of barium dioxide) is measured off for assay.

Drop into this from a burette, with constant stirring, decinormal potassium permanganate V. S. until a final drop gives the solution a permanent pink tint.

Not less than 40 cc. of the decinormal permanganate V. S. should be required to produce this result.

In this process, the first step is the formation of hydrogen peroxide by treating the barium peroxide with phosphoric acid, as illustrated by the following equation:



The hydrogen peroxide is then estimated with decinormal permanganate V. S.



$$\begin{array}{r} 100)169.6 \\ 100)1.70 \\ \quad *1.70 \end{array} \quad \begin{array}{r} 100)315.34 \\ 3.1534 \text{ gms. or } 1000 \text{ cc.} \end{array} \quad \frac{\text{N}}{10} \text{ permanganate V. S.}$$



Thus each cc. of  $\frac{\text{N}}{10}$  potassium permanganate V. S. represents 0.001696 gm. (\*0.0017 gm.) of  $\text{H}_2\text{O}_2$ ; and since 169.6 gms. of  $\text{H}_2\text{O}_2$  are equivalent to 844.1 gms. of  $\text{BaO}_2$ ,  $\left( \frac{5\text{BaO}_2 = 5\text{H}_2\text{O}_2}{844.1 \text{ gms. } 169.6 \text{ gms.}} \right)$ , 1 cc. of the  $\frac{\text{N}}{10}$  permanganate solution corresponds to 0.008441 gm. of  $\text{BaO}_2$ .

Not less than 40 cc. of the decinormal solution should be required.

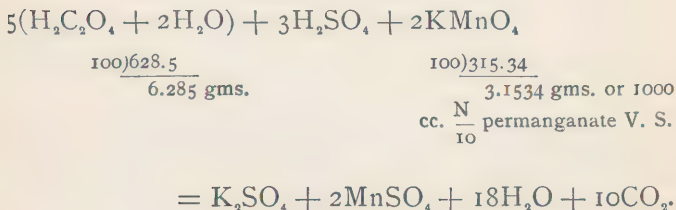
$$\text{Thus } .008441 \times 40 = 0.3376 \text{ gm.}$$

$$\frac{.3376 \times 100}{.422} = 80\% \text{ of pure BaO}_2.$$

**Oxalic Acid,**  $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} = \left\{ \begin{array}{l} 125.7. \\ *126 \end{array} \right.$  — Oxalic acid may be estimated either by neutralization with an alkaline V. S., or by oxidation with potassium permanganate V. S.

The permanganate is generally used when the acid is in combination as oxalate.

The reaction is illustrated as follows :



Thus each cc. of the  $\frac{\text{N}}{10}$  permanganate represents 0.006285 gm. of pure oxalic acid (crystallized).

*Note.*—It must be remembered, in titrating with permanganate, that an excess of sulphuric acid is always necessary, in order to keep the resulting manganous compound in solution, by forming a soluble manganous sulphate.

If hydrochloric acid is used the solution must be very dilute, and the temperature not raised too high, otherwise chlorine will be liberated, which will spoil the analysis.

It should be borne in mind that the solution of potassium permanganate should not be filtered through paper, as it is decomposed by organic matter. It may, however, be filtered through gun-cotton or glass-wool. It should never be used in a Mohr's burette.



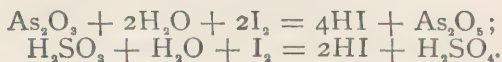
## CHAPTER XII.

## ANALYSIS BY INDIRECT OXIDATION.

THIS method of analysis is based upon the oxidizing power of iodine.

Iodine acts upon the elements of water, forming hydriodic acid with the hydrogen, and liberating oxygen in a nascent state.

Nascent oxygen is a very active agent, and readily combines with and oxidizes many substances, such as arsenous oxide, sulphurous acid, sulphites, thiosulphates, etc.



Therefore iodine is said to be an indirect oxidizer, and may be used for the estimation of a great variety of substances, with extreme accuracy.

The end of the reaction in an analysis by this method is ascertained by the use of starch test solution, which produces, with the slightest trace of free iodine, a distinct blue color.

In making an analysis with standard iodine solution, the substance under examination is brought into dilute solution, the starch solution added, and then the iodine, in the form of a decinormal solution, is delivered in from a burette, stirring or shaking constantly, until a final



drop colors the solution blue—a sign that a slight excess of iodine has been added.

**Decinormal Iodine V. S., I** =  $\left\{ \begin{array}{cc} 126.53 & 12.653 \\ *_{126.5} & *_{12.65} \end{array} \right\}$

in 1 litre.—12.653 gms. of pure iodine are dissolved in 300 cc. of distilled water containing 18 gms. of pure potassium iodide. Then enough water is added to make the solution measure, at 15° C. (59° F.), exactly 1000 cc. The solution should be kept in small glass-stoppered vials, in a dark place.

The potassium iodide used in this solution acts merely as a solvent for the iodine.

If pure iodine be not at hand, it may be prepared from the commercial article as follows :

Powder the iodine and heat it in a porcelain dish placed over a water-bath, stirring constantly with a glass rod for 20 minutes. Any adhering moisture, together with any cyanogen iodide, and most of the iodine bromide and iodine chloride, is thus vaporized.

Then triturate the iodine with about 5 per cent. of its weight of pure, dry potassium iodide. The iodine bromide and chloride are thereby decomposed, potassium bromide and chloride being formed, and iodine liberated from the potassium iodide.

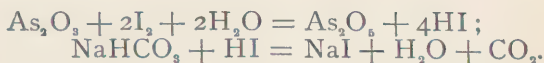
The mixture is then returned to the porcelain dish, covered with a clean glass funnel, and heated on a sand-bath. A pure resublimed iodine is then obtained.

If pure iodine is used in making this solution, there is no necessity for checking (standardizing) it.

But if desired, the solution may be checked against pure arsenous acid or pure sodium thiosulphate,

## ESTIMATION OF ARSENOUS ACID.

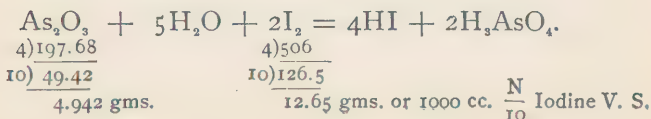
**Arsenous Anhydride**, Arsenic Trioxide,  $\text{As}_2\text{O}_3 = \left\{ \begin{array}{l} 197.68 \\ *198 \end{array} \right.$ .—When arsenous acid is brought in contact with iodine in the presence of water and an alkali, it is oxidized into arsenic acid, and the iodine is decolorized. The reaction is:



The alkali should be in sufficient quantity to combine with the hydriodic acid formed, and must be in the form of potassium or sodium bicarbonate.

The hydroxides or carbonates should not be used, as they interfere with the indicator. Starch solution is used as the indicator, a blue color being formed as soon as the arsenous acid is entirely oxidized into arsenic acid.

0.1 gm. of arsenous acid is accurately weighed and dissolved, together with about 1 gm. of sodium bicarbonate, in 20 cc. of water heated to boiling. Allow the liquid to cool, add a few drops of starch T. S., and allow the decinormal iodine V. S. to flow in, shaking or stirring the mixture constantly, until a permanent blue color is produced. The following equation illustrates the reaction :



Thus it is seen that each cc. of the  $\frac{N}{10}$  standard solution represents 0.004942 gm. of pure  $As_2O_3$ .

If 20 cc. are consumed, then

$$\begin{aligned} 0.004942 \times 20 &= 0.09884 \text{ gm.} \\ \frac{.09884 \times 100}{.1} &= 98.84\% \end{aligned}$$

The U. S. P. requirement is 98.8% of  $As_2O_3$ . The starch T. S. is not used in the U. S. P. process, and the end of the reaction is known by the iodine being no longer decolorized. But with starch the indication is exceedingly delicate, and it should always be used.

**Liquor Acidi Arsenosi, U. S. P.**—Measure accurately 10 cc. of the solution, add to it 1 gm. of sodium bicarbonate, and boil for a few minutes. Then allow the liquid to cool, and dilute it to 50 cc. with water. A little starch T. S. is then added and the decinormal iodine V. S. run in from a burette, until a final drop produces the blue color of starch iodide.

Each cc. of  $\frac{N}{10}$  I. V. S. represents 0.004942 gm. of  $As_2O_3$ . (See Estimation of Arsenous Acid.)

The U. S. P. requirement is that 24.7 cc. of the *liquor acidi arsenosi*, when treated as above, will consume 49.4 to 50 cc. of decinormal iodine V. S. Use 2 gms. of the bicarbonate.

$$0.004942 \times 50 = 0.2471 \text{ gm.}$$

$$\frac{0.2471 \times 100}{24.7} = 1\%$$

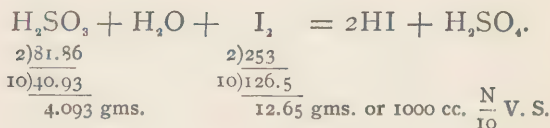
**Liquor Potassii Arsenitis, U. S. P.** (Fowler's Solution).—The process is exactly the same as the foregoing. 24.7 cc., diluted and treated with 2 gms. of sodium bicarbonate, should require 49.4 to 50 cc. of the  $\frac{N}{10}$  I. V. S., corresponding to 1% of  $As_2O_3$ .

**Sulphurous Acid** (Acidum Sulphurosum, U. S. P.)—This is an aqueous solution of sulphur dioxide,  $SO_2 = \begin{cases} 63.9 \\ *64 \end{cases}$ , containing 6.4 per cent., by weight, of the gas.

Sulphurous acid when brought in contact with iodine is oxidized into sulphuric, the iodine being decolorized because of its union with the hydrogen of the accompanying water, forming hydriodic acid.

Two gms. of sulphurous acid are taken and diluted with distilled water (recently boiled and cooled) to about 25 cc. The decinormal iodine V. S. is then delivered into the solution (to which a little starch T. S. had been previously added) until a permanent blue color is produced. At least 40 cc. of the standard iodine solution should be consumed before this color appears.

The following equations, etc., show the reaction that takes place :



Thus each cc. of the  $\frac{N}{10}$  V. S. represents .004093 gm. of pure  $H_2SO_3$ .

Sulphurous acid being, however, looked upon as a

solution of  $\text{SO}_2$  in water, the quantity of this gas is generally estimated in analysis.



$$\begin{array}{r} 2)63.9 \\ 10)31.95 \end{array}$$

3.195 gms.

$$\begin{array}{r} 2)253 \\ 10)126.5 \end{array}$$

12.65 gms.

Thus each cc. of  $\frac{\text{N}}{10}$  V. S. consumed before the blue color appears represents 0.003195 gm. of  $\text{SO}_2$ .

If 40 cc. are consumed in the above analysis, the 2 gms. contain

$$0.003195 \times 40 = 0.1278;$$

then

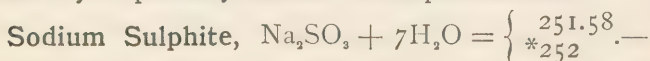
$$\frac{0.1278 \times 100}{2} = 6.39\% \text{ of } \text{SO}_2.$$

The sulphurous acid should be diluted with distilled water to below 0.04 per cent before titrating it; for if it is not sufficiently diluted there is a risk of the sulphuric acid formed, being again reduced to sulphurous, with liberation of iodine, thus causing irregular results.

This may, however, be obviated by adding at once a measured excess of  $\frac{\text{N}}{10}$  iodine V. S. and titrating back

with  $\frac{\text{N}}{10}$  sodium thiosulphate V. S.

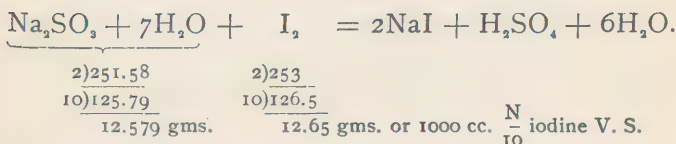
The direction to boil the distilled water is given for the purpose of freeing it from air, which would have a tendency to partially oxidize the sulphurous acid.



One gm. of the salt is dissolved in 25 cc. of distilled

water recently boiled to expel air, a little starch T. S. is added, and then the decinormal iodine V. S. delivered in from a burette, until the blue color of starch iodide appears, which does not disappear upon shaking or stirring.

The reaction is expressed as follows :



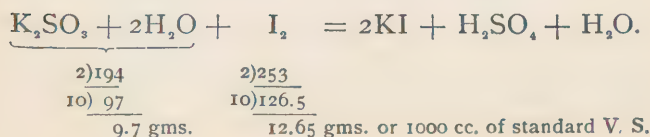
Thus each cc. of the standard solution represents .012579 gm. of crystallized sodium sulphite.

If 1 gm. of the salt is taken, to find the percentage multiply the factor by the number of cc. of standard solution consumed, and the result by 100.

The U. S. P. requirement is 96 per cent. 0.63 gm. of salt should require for complete oxidation 48 cc. of the standard solution. Therefore

$$\begin{aligned} .012579 \times 48 &= .603792 \text{ gm.} \\ \frac{.603792 \times 100}{0.63} &= 95.8\% \end{aligned}$$

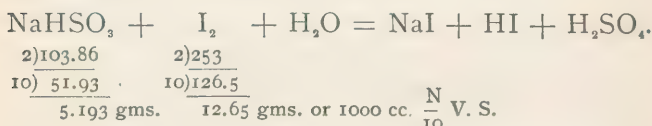
**Potassium Sulphite,**  $\text{K}_2\text{SO}_3 + 2\text{H}_2\text{O} = *194$ .—Operate upon 0.5 gm. in the same manner as for sodium sulphite.



Each cc. of the decinormal iodine V. S. used represents 0.0097 gm. of crystallized potassium sulphite. If 46 cc. are used, the salt is over 89% strength.

**Sodium Bisulphite**,  $\text{NaHSO}_3 = \left\{ \begin{array}{l} 103.86 \\ *104 \end{array} \right.$ .—Dissolve 0.26 gm. of the salt in 20 cc. of distilled water which has been previously boiled to expel air, add a little starch T. S., and pass in the decinormal iodine V. S. from a burette, until a permanent blue color appears. At least 45 cc. should be required.

Apply the following equation :



Thus each cc. of decinormal iodine V. S. represents 0.005193 gm. of sodium bisulphite.

$$0.005193 \times 45 = 0.23368 \text{ gm.}$$

$$\frac{0.23368 \times 100}{0.26} = 89.5\%$$

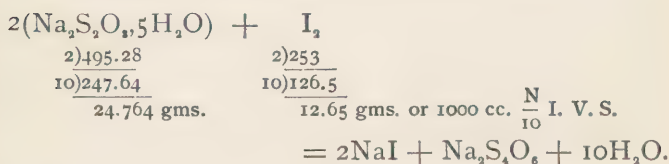
**Sodium Thiosulphate** (Sodium Hyposulphite),  $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O} = \left\{ \begin{array}{l} 247.64 \\ *248 \end{array} \right.$ .—This salt, when brought in contact with iodine, is converted into tetrathionate of sodium, and the iodine is decolorized.

It is estimated as follows: 0.25 gm. of the salt is dissolved in 10 cc. of water, a few drops of starch T. S. are added, and then the  $\frac{\text{N}}{10}$  iodine V. S. is delivered in from a burette, until the appearance of blue starch iodide indicates an excess of iodine.



At least 9.9 cc. of the standard solution should be added before a final drop produces a permanent blue color.

The reaction is expressed as follows :



Thus each cc. represents .024764 gm. of crystallized thiosulphate.

9.9 cc. contain 0.024764 gm.  $\times 9.9 = .2451636$  gm.

$$\frac{0.2451636 \times 100}{0.25} = 98.1\%$$

Iodine may also be used for estimating antimonous compounds. The reaction is similar to that with arsenous compounds; thus

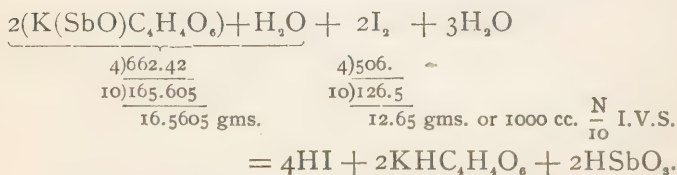


**Antimony and Potassium Tartrate** (Tartar Emetic),  $2(\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6) + \text{H}_2\text{O} = \left\{ \begin{array}{l} 662.42 \\ *664 \end{array} \right.$ .—This is the only antimonial salt, a process for the volumetric estimation of which is given in the U. S. P.

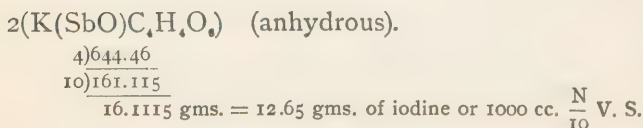
The U. S. P. directs that 0.331 gm. of the crystallized salt or 0.322 gm. of the salt dried at  $110^\circ \text{C}$ . ( $230^\circ \text{F}$ .) be taken for analysis. The salt is dissolved in 10 cc. of water, and about 20 cc. of a cold saturated solution of sodium bicarbonate and a little starch T. S. added. The decinormal iodine V. S. is then delivered in from a burette, until the blue color of the starch

iodide makes its appearance, indicating that the salt has been completely oxidized and that the iodine solution has been added in slight excess. Not less than 20 cc. of decinormal iodine V. S. should be consumed before the blue color appears.

The reaction is illustrated by the following equation :



Thus each cc. of  $\frac{\text{N}}{10}$  iodine V. S. represents 0.0165605 gm. of pure *crystallized* tartar emetic.



Thus each cc. of  $\frac{\text{N}}{10}$  iodine V. S. represents 0.0161115 gm. of *anhydrous* tartar emetic. Thus

$$20 \text{ cc.} = 0.0165605 \text{ gm.} \times 20 = .33121 \text{ gm.};$$

$$\frac{0.33121 \times 100}{0.331} = 100\% \text{ crystallized salt};$$

and

$$0.0161115 \times 20 = 0.32223 \text{ gm.}$$

$$\frac{0.32223 \times 100}{0.322} = 100\% \text{ anhydrous salt.}$$

The operation should be quickly conducted or a precipitate of antimonous hydrate will be formed, upon which the iodine has little effect. The antimony must be in solution to be properly attacked.

TABLE OF SUBSTANCES ESTIMATED BY IODINE.

Name of Substance.	Formula.	Molecular Weight.	Factor.
Antimony and potassium tartrate.....	$2(\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6) + \text{H}_2\text{O}$	662.42	{ Cryst. .016560 Anhydr. .016111
Arsenic trioxide.....	$\text{As}_2\text{O}_3$	197.68	.004942
Potassium sulphite.....	$\text{K}_2\text{SO}_3 + 2\text{H}_2\text{O}$	193.84	.009692
Sodium bisulphite.....	$\text{NaHSO}_3$	103.86	.005193
Sodium sulphite.....	$\text{Na}_2\text{SO}_3 + 7\text{H}_2\text{O}$	251.58	.012579
Sodium thiosulphate (hyposulphite).....	$\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$	247.64	.024764
Sulphur dioxide.....	$\text{SO}_2$	63.90	.003195
Sulphurous acid.....	$\text{H}_2\text{SO}_3$	81.86	.004093

## CHAPTER XIII.

## ESTIMATION OF SUBSTANCES READILY REDUCED.

ANY substance which readily yields oxygen in a definite quantity, or is susceptible of an equivalent action, which involves its reduction to a lower quantivalence, may be quantitatively tested, by ascertaining how much of a reducing agent of known power is required by a given quantity of the substance for its complete reduction.

The principal reducing agents which may be employed in volumetric analysis are *sodium thiosulphate*, sulphurous acid, arsenous acid, oxalic acid, metallic zinc, and magnesium.

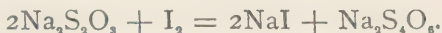
The sodium thiosulphate is the only one which is employed officially in the U. S. P. in the form of a volumetric solution. It is used in the estimation of free iodine, and indirectly of other free halogens, or compounds in which the halogen is easily liberated, as in the hypochlorites, etc.

This method of analysis is called *Iodometry*.

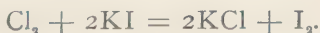
It depends upon the fact that iodine is an indirect oxidizer, as shown by its action upon water, the hydrogen of which it abstracts, forming hydriodic acid, thus liberating the oxygen in a nascent state.

When sodium thiosulphate acts upon iodine, sodium tetrathionate and sodium iodide are formed, and the solution is decolorized.

This reaction takes place in definite proportions: one molecular weight of the thiosulphate, absorbs one atomic weight of iodine.



Chlorine cannot be directly titrated with the thiosulphate, but by adding to the solution containing free chlorine an excess of potassium iodide, the iodine is liberated in exact proportion to the quantity of chlorine present, atom for atom.



Then by estimating the iodine, the quantity of chlorine is ascertained. All bodies which contain available chlorine, or which when treated with hydrochloric acid evolve chlorine, may be estimated by this method.

Also, bodies which contain *available oxygen*, and which when boiled with hydrochloric acid evolve chlorine, such as *manganates, chromates, peroxides*, etc., may be estimated in this way.

Solutions of *ferric salts*, when acidulated and boiled with an excess of potassium iodide, liberate iodine in exact proportion to the quantity of ferric iron present.

Thus sodium thiosulphate may be used in the estimation of a great variety of substances with extreme accuracy.

### Preparation of Decinormal Sodium Thiosulphate

(Hyposulphite),  $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O} = \left\{ \begin{array}{l} 247.64 \\ *248 \end{array} \right\}$  contains

$\left\{ \begin{array}{l} 24.746 \\ *24.8 \end{array} \right\}$  gms. in 1 litre.—Sodium thiosulphate is a salt of thiosulphuric acid in which two atoms of hydrogen have been replaced by sodium; it therefore seems that a

normal solution of this salt should contain one half the molecular weight in grammes in one litre.

But this salt is used chiefly for the estimation of iodine, and, as stated before, one full molecular weight reacts with and decolorizes one atomic weight of iodine; and since one atom of iodine is chemically equivalent to one atom of hydrogen, a full molecular weight of sodium thiosulphate, must be contained in a litre of its normal solution.

Sodium thiosulphate is easily obtained in a pure state, and therefore the proper weight of the salt, reduced to powder and dried between sheets of blotting-paper, may be dissolved directly in water, and made up to one litre.

The U. S. P. directs that a stronger solution than necessary be made, its titer found by iodine, and then the solution diluted to the proper measure.

30 gms. of selected crystals of the salt are dissolved in enough water to make, at or near 15° C. (59° F.) 1100 cc.

Transfer 10 cc. of this solution into a flask or beaker, add a few drops of starch T. S., and then gradually deliver into it from a burette decinormal iodine solution, in small portions at a time, shaking the flask after each addition, and regulating the flow to drops toward the end of the operation. As soon as a blue color is produced which does not disappear upon shaking, but is not deeper than pale blue, the reaction is completed. Note the number of cc. of iodine solution used, and then dilute the thiosulphate solution so that equal volumes of it and the decinormal iodine V. S. will exactly correspond to each other, under the above-mentioned conditions.

*Example.*—The 10 cc. of sodium thiosulphate, we will assume, require 10.7 cc. of decinormal iodine V. S.

The sodium-thiosulphate solution must then be diluted in the proportion of 10 cc. to 10.7 cc., or 1000 cc. to 1070 cc.

After the solution is thus diluted a new trial should be made, in the manner above described, in which 50 cc. of the thiosulphate solution should require exactly 50 cc. of the decinormal iodine V. S. to produce a faint-blue color.

The solution should be kept in small dark amber-colored, glass-stoppered bottles, carefully protected from dust and air.

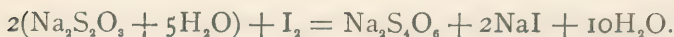
One cc. of this solution is the equivalent of :

Iodine.....	0.012653 gramme.
Bromine.....	0.007976 “
Chlorine.....	0.003537 “
Iron in ferric salts.....	0.005588 “

**Iodine, I** =  $\left\{ \begin{array}{l} 126.53 \\ *126.5 \end{array} \right.$ .—Dissolve 0.32 gm. of iodine in 20 cc. of water, in a beaker or flask, with the aid of 1 gm. of potassium iodide; the solution is mixed with a few drops of starch T. S., and then the decinormal sodium thiosulphate V. S. gradually delivered in from a burette, in small portions at a time, shaking the flask after each addition, and regulating the flow to drops toward the end of the reaction, until a final drop just discharges the blue color.

Note the number of cc. of decinormal sodium thiosulphate V. S. consumed, and multiply this number by the factor for iodine.





$$\begin{array}{r} 2)496 \\ 10)248 \\ \hline 24.8 \text{ gms. or} \\ 1000 \text{ cc. } \frac{\text{N}}{10} \text{ V. S.} \end{array} \qquad \begin{array}{r} 2)253 \\ 10)126.5 \\ \hline 12.65 \text{ gms.} \end{array}$$

Thus the factor for iodine, that is, the quantity equivalent to 1 cc. of  $\frac{\text{N}}{10}$  thiosulphate V. S., is 0.01265 gm.

0.32 gm. of iodine, which answers to the tests of the U. S. P., requires at least 25 cc. of the  $\frac{\text{N}}{10}$  V. S.

$$\begin{aligned} 0.01265 \times 25 &= 0.31625 \text{ gm.} \\ \frac{.31625 \times 100}{.32} &= 98.8\% \text{ pure iodine.} \end{aligned}$$

**Liquor Iodi Compositus** (Lugol's Solution).—This is an aqueous solution of iodine and potassium iodide.

It is estimated for iodine in the same way as the foregoing. The potassium iodide acts merely as a solvent for free iodine, and does not enter into the reaction.

10 or 12 gms. of the solution is a convenient quantity to operate upon. Starch T. S. is the indicator.

The U. S. P. states that 12.66 gms. of the solution should require for complete decoloration from 49.3 to 50 cc. of decinormal sodium thiosulphate V. S.

As shown by the above equation, each cc. of the  $\frac{\text{N}}{10}$  V. S. represents 0.01265 gm. of pure iodine. Therefore 50 cc. represent  $0.01265 \times 50 = .6325$  gm.

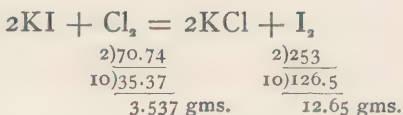
$$\frac{.6325 \times 100}{12.66} = 5\% \text{ pure iodine, about.}$$

**Tinctura Iodi** (Tincture of Iodine).—This is an alcoholic solution of free iodine, and must be diluted with a solution of potassium iodide, before titration, in order to provide sufficient liquid to keep the resulting salts in solution.

**Aqua Chlorig** (Chlorine Water).—This is an aqueous solution of chlorine,  $\text{Cl} = \left\{ \begin{array}{l} 35.37 \\ *35.4 \end{array} \right.$ , containing at least 0.4% of the gas.

The estimation of chlorine is effected in an indirect way, namely, by determining the quantity of iodine which it liberates from potassium iodide.

A definite quantity of chlorine will liberate a definite quantity of iodine from an iodide; these quantities are in exact proportion to their atomic weights, as the equation shows:

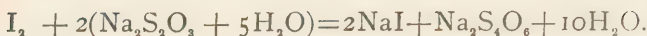


Thus it is seen that by estimating the liberated iodine the quantity of chlorine may be determined with accuracy.

Ten gms. is a convenient quantity to operate upon. To this about half a gramme of potassium iodide is added. A little starch T. S. is then introduced, and the titration is begun, with decinormal sodium thiosulphate V. S.

When the blue color of starch iodide has entirely disappeared the reaction is finished.

The reaction between iodine and sodium thiosulphate is illustrated by the following equation:



$$\begin{array}{r} 2)253 \\ 10)126.5 \\ \hline 12.65 \text{ gms.} \end{array} \qquad \begin{array}{r} 2)496 \\ 10)248 \\ \hline 24.8 \text{ gms. or } 1000 \text{ cc. } \frac{N}{10} \text{ V. S.} \end{array}$$

Thus we see that 1000 cc. of  $\frac{N}{10}$   $Na_2S_2O_3 \cdot 5H_2O$  represent 12.65 gms. of iodine, which are equivalent to 3.537 gms. of chlorine.

Each cc. therefore is equivalent to .003537 gm. of chlorine. This number is the factor which, when multiplied by the number of cc. of  $\frac{N}{10}$  thiosulphate V. S. used, gives the weight in grammes of chlorine, contained in the quantity of chlorine water acted upon.

The U. S. P. requirement is that 17.7 gms. of chlorine water, when mixed with 1 gm. of potassium iodide dissolved in 10 cc. of water, and titrated with  $\frac{N}{10}$  sodium thiosulphate V. S. should consume not less than 20 cc. of the latter in decolorizing the solution.

$$.003537 \times 20 = .07074 \text{ gm.}$$

$$\frac{.07074 \times 100}{17.7} = .04\% \text{ of chlorine.}$$

**Chlorinated Lime** (Calx Chlorata, Chloride of Lime, Bleaching-powder).—This substance was formerly supposed to be a compound of lime and chlorine,  $CaOCl_2$ , and hence the name chloride of lime. It is now generally considered to be a mixture of calcium chloride and

calcium hypochlorite,  $\text{CaCl}_2 + \text{Ca}(\text{ClO})_2$  or  $2(\text{CaOCl}_2)$ . The hypochlorite is the active constituent. This is a very unstable salt, and is readily decomposed even by carbonic acid. When treated with hydrochloric acid it gives off chlorine.

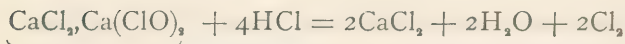
The value of chlorinated lime as a bleaching or disinfecting agent depends upon its available chlorine, that is, the chlorine which the hypochlorite yields when treated with an acid.

In estimating the available chlorine, the latter is liberated with hydrochloric acid. This liberated gas, then, acting upon potassium iodide, sets free an equivalent amount of iodine. The quantity of iodine is then determined, and thus the amount of available chlorine found. .1 to .2 gm. is a convenient quantity to operate upon.

The U. S. P. directs to weigh off \*.35 (0.354) gm. of chlorinated lime. This is to be thoroughly triturated with 50 cc. of water and carefully transferred, together with the washings into a flask. 0.8 gm. or more of potassium iodide and 5 cc. of diluted hydrochloric acid are then added, and into the resulting reddish-brown liquid,

the  $\frac{\text{N}}{10}$  sodium thiosulphate V. S. is delivered from a burette. Towards the end of the titration, when the brownish color of the liquid is very faint, a few drops of starch T. S. are added and the titration continued until the bluish or greenish color produced by the starch has entirely disappeared. Not less than 35 cc. of the volumetric solution should be required to produce this result.

The reactions which take place in this process are illustrated by the following equations :

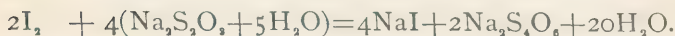


$$\begin{array}{r} 4) 141.48 \\ 10) 35.37 \\ \hline \end{array}$$

3.537 gms.

$$\begin{array}{r} 4) 506 \\ 10) 126.5 \\ \hline \end{array}$$

12.65 gms.



$$\begin{array}{r} 40) 506 \\ \hline \end{array}$$

12.65 gms.

$$\begin{array}{r} 40) 196 \\ \hline \end{array}$$

24.8 gms. or 1000 cc.

 $\frac{N}{10}$  thiosulphate V. S.

We thus see that 1 cc. of the decinormal volumetric solution represents 0.01265 gm. of iodine, which is equivalent to 0.003537 gm. of available chlorine. Then

$$0.003537 \times 35 = 0.12379 \text{ gm.}$$

$$\frac{0.12379 \times 100}{.35} = 35\% \text{ of available chlorine.}$$

This is a very rapid method for estimating chlorine; but when calcium chlorate is present in the bleaching-powder (and it often is, through imperfect manufacture) the chlorine from it, is recorded, as well as that from the hypochlorite, the chlorate being decomposed into chlorine, etc., by hydrochloric acid. The chlorate, however, is of no value in bleaching; its chlorine is not available. Hence, unless the powder is known to be free from chlorate, the analysis should be made by means of arsenous-acid solution.

**The Arsenous-acid Process.**—0.35 gm. of the bleaching-powder is rubbed to a smooth paste with 50 cc. of water, as described above. A measured excess of decinormal arsenous acid V. S. is then added; this

is followed by a little starch T. S., and then decinormal iodine V. S. added until the blue color appears. Deduct the number of cc. of the standard iodine solution used from those of standard arsenous-acid solution, and the quantity of the latter which went into combination is found.

Each cc. of  $\frac{N}{10}$   $As_2O_3$  V. S. represents .003537 gm. of available chlorine.

$$\begin{array}{rcl}
 2CaOCl_2 + As_2O_3 & = & As_2O_5 + 2CaCl_2 \\
 \begin{array}{r} 4)141.48 \\ 10) 35.37 \\ \hline 3.537 \text{ gms.} \end{array} & & \begin{array}{r} 4)198 \\ 10) 49.5 \\ \hline 4.95 \text{ gms. or } 1000 \text{ cc.} \end{array} \frac{N}{10} \text{ V. S.}
 \end{array}$$

**Decinormal Arsenous-acid Solution** is made by dissolving 4.95 gms. of the purest sublimed arsenous anhydride ( $As_2O_3$ ) in about 250 cc. of distilled water with the aid of about 20 gms. of pure potassium bicarbonate. The acid should be in fine powder, and the mixture warmed, to effect complete solution.

The solution is checked with decinormal iodine V. S., using starch as indicator.

Decinormal arsenous-acid solution and decinormal iodine solution should correspond, volume for volume.

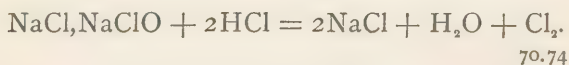
**Liquor Sodæ Chloratæ** (Solution of Chlorinated Soda; Labarraque's Solution).—This is an aqueous solution of several chlorine compounds of sodium, principally sodium chloride and hypochlorite, containing at least 2.6% of available chlorine.

In this solution, as in chlorinated lime, it is the available chlorine which is estimated. The chlorine is first liberated with hydrochloric or sulphuric acid; this then liberates iodine from potassium iodide, and the

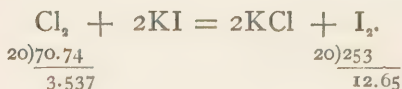
free iodine is then determined by standard solution of thiosulphate.

\*6.7 (6.74) gms. of chlorinated soda solution are mixed with 50 cc. of water, 2 gms. of potassium iodide, and 10 cc. of hydrochloric acid, together with a few drops of starch T. S. Then pass into the mixture from a burette sufficient decinormal sodium thiosulphate V. S. to just discharge the blue or greenish tint of the liquid.

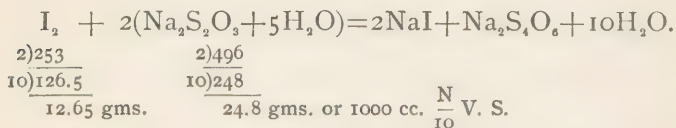
The reaction is illustrated by the following equation. Hydrochloric acid liberates chlorine from the salts in the solution :



The chlorine then liberates iodine from potassium iodide :



The iodine is then determined by sodium thiosulphate V. S. :



Thus each cc. of standard solution represents .01265 gm. of iodine, which is equivalent to .063537 gm. of available chlorine.

In practice the potassium iodide should always be added before the hydrochloric acid is, so that the



chlorine has potassium iodide to act upon, as soon as it is itself liberated, and thus any loss of chlorine is obviated.

In the pharmacopœial test above given not less than 50 cc. of the  $\frac{N}{10}$  V. S. should be required.

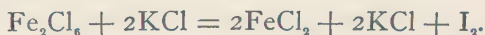
$$0.003537 \times 50 = 0.17785 \text{ gm.}$$

$$\frac{0.17785 \times 100}{6.7} = 2.65\% \text{ available Cl.}$$

Instead of weighing off the U. S. P. quantity, any other convenient weight may be taken.

#### ESTIMATION OF FERRIC SALTS.

When a ferric salt in an acidulated solution is digested with an excess of potassium iodide the salt is reduced to the ferrous state, and iodine is set free.



One atom of iodine is liberated for each atom of iron in the ferric state. The liberated iodine is then determined by sodium thiosulphate, in the usual way. 12.65 gms. of iodine = 5.6 gms. of metallic iron.

This is the method of the U. S. P.; it is given in detail here.

\*0.56 (0.5588) gm. of the salt is dissolved in 10 or 15 cc. of water and 2 cc. of hydrochloric acid in a glass-stoppered bottle having a capacity of about 100 cc. 1 gm. of potassium iodide is then added, and the mixture digested for half an hour at a temperature of 40° C. (104° F.). During the digestion the stopper should be

left in the bottle, and the heat not allowed to rise too high, otherwise the liberated iodine will be volatilized. When cool a few drops of starch T. S. are added. It is now ready for titrating with  $\frac{N}{10}$  sodium thiosulphate. Each cc. corresponds to 1 per cent. of metallic iron.

When the quantity of metallic iron and the chemical formula for the ferric salt under estimation are known, the quantity of pure salt is easily found by calculation.

In all the estimations of ferric iron it is convenient to take 0.56 gm. of the salt. Each cc. of the volumetric solution used will then represent 1% of metallic iron, assuming the atomic weight of iron to be 56.

Ferric salts may be tested in many other ways; for instance:

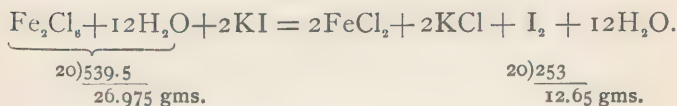
A ferric salt in solution may be filtered through a column of zinc dust, which reduces it to the ferrous state. This is then estimated with potassium permanganate V. S. in the usual method, or the ferric solution is treated with a few small pieces of zinc or magnesium coarsely powdered, until complete reduction is effected. When a red color is no longer produced by sulphocyanate of potassium the ferric salt is completely reduced, and may be estimated with potassium permanganate V. S.

Stannous chloride, ammonium bisulphite, and other substances may also be used as reducing agents.

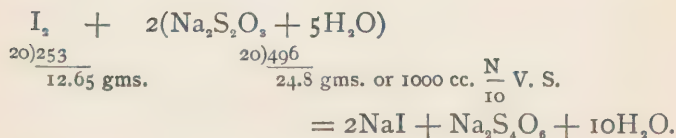
**Ferric Chloride,**  $\text{Fe}_2\text{Cl}_6 + 12\text{H}_2\text{O} = \left\{ \begin{array}{l} 539.5 \\ *540.4 \end{array} \right.$ —  
 \*0.56 (0.5588) gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of about 100 cc.) in 10 cc. of water and 2 cc. of hydrochloric acid, and

after the addition of 1 gm. of potassium iodide, is kept for half an hour at a temperature of 40° C. (104° F.), then cooled, mixed with a few drops of starch T. S., and titrated with decinormal sodium thiosulphate V. S. until the blue or greenish color of the liquid is discharged. Each cc. represents \*0.0056 gm. or 1% of metallic iron, or 0.026975 gm. of pure ferric chloride.

The following equations illustrate the reactions:



Then



20 cc. of the  $\frac{\text{N}}{10}$  V. S. should be required, which represents 20% of metallic iron, or 96.34% of pure ferric chloride (crystallized):

$$\begin{array}{l} 0.026975 \times 20 = 0.5395 \text{ gm.} \\ \frac{0.5395 \times 100}{0.56} = 96.34\% \end{array}$$

**Liquor Ferri Chloridi** (Solution of Ferric Chloride).

—This is an aqueous solution of ferric chloride,  $\text{Fe}_2\text{Cl}_6$

$= \left\{ \begin{array}{l} 323.98 \\ *324.4 \end{array} \right.$ , containing about 37.8 per cent. of the anhydrous salt or about 13 per cent. of metallic iron.

0.56 (or .5588) gm. of the solution is introduced into a glass-stoppered bottle (having a capacity of about 100 cc.), together with 15 cc. of water and 2 cc. of hydrochloric acid. 1 gm. of potassium iodide is then added, and the mixture kept for half an hour at 40° C. (104° F.), then cooled, and mixed with a few drops of starch T. S. and titrated with  $\frac{N}{10}$  sodium thiosulphate V. S.

until the blue or greenish color of the liquid is discharged. 0.56 gm. of the solution having been taken, each cc. of the standard solution represents 1 per cent. and 13 cc. should be required. If 1.12 gms. are taken, as the U. S. P. directs, each cc. represents 0.5 per cent. and 26 cc. should be required. The reactions are the same as in ferric chloride, each cc. representing 0.026975 gm. of crystallized ferric chloride, or 0.016199 gm. of anhydrous ferric chloride, or .0056 gm. of metallic iron. To find percentage: Multiply by number of cc. used, then multiply the result by 100 and divide by the quantity of solution taken.

**Tinctura Ferri Chloridi** (Tincture of Ferric Chloride).—A hydro-alcoholic solution of ferric chloride,  $\text{Fe}_2\text{Cl}_6 = \left\{ \begin{array}{l} 323.98 \\ *324.4 \end{array} \right.$ , containing about 13.6 per cent. of anhydrous ferric chloride, and corresponding to about 4.7 (4.69) per cent. of metallic iron.

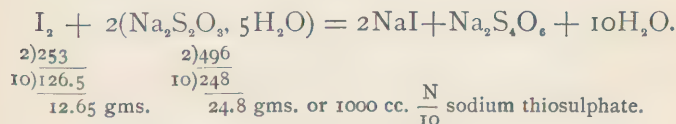
To estimate this tincture follow the directions given for *liquor ferri chloridi*.

**Ferric Citrate**,  $\text{Fe}_2(\text{C}_6\text{H}_5\text{O}_7)_2 = \left\{ \begin{array}{l} 488.48 \\ *490 \end{array} \right.$ .—\*0.56 (0.5588) gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of 100 cc.) in 15 cc. of water and 2 cc. of hydrochloric acid, with the aid of gentle heat. 1 gm. of potassium iodide is then added,

and the mixture kept for half an hour at a temperature of  $40^{\circ}$  C. ( $104^{\circ}$  F.). It is then cooled, and a few drops of starch T. S. added. The decinormal sodium thio-sulphate V. S. is then delivered in from a burette, until the blue or greenish color of the liquid just disappears. Each cc. of the decinormal solution represents 1 per cent. or 0.0056 gm. of metallic iron, corresponding to 0.024424 gm. of ferric citrate.



Ferric citrate.	Ferrous citrate.	
3Fe <sub>2</sub>	488.48	
6)335.28	3	6)759
10)55.88	6)1465.44	10)126.5
5.588 gms.	244.24	12.65 gms.
(*5.6 gms.)	24.424 gms.	



Thus each cc. represents 0.01265 gm. of iodine, which corresponds to 0.024424 gm. of ferric citrate or \*0.0056 gm. metallic iron.

$$16 \text{ cc.} = 16 \times 0.0056 = 0.896 \text{ gm. metallic iron.}$$

$$\frac{0.896 \times 100}{0.56} = 16\%$$

$$16 \times 0.024424 = 0.390784 \text{ gm. ferric citrate.}$$

$$\frac{0.390784 \times 100}{0.56} = 69.9\%$$

### Liquor Ferri Citratis (Solution of Ferric Citrate).

—This is an aqueous solution of ferric citrate, corresponding to about 7.5 per cent. of metallic iron.

\*0.56 (0.5588) gm. of the solution is introduced into a glass-stoppered bottle (having a capacity of about 100 cc.), together with 15 cc. of water and 2 cc. of hydrochloric acid. 1 gm. of potassium iodide is then added, and the mixture kept at a temperature of 40° C. (104° F.) for half an hour; it is then cooled and mixed with a few drops of starch T. S., and decinormal thiosulphate V. S. delivered in from a burette until the blue or greenish color of the liquid is discharged. Each cc. of the volumetric solution indicates 1% of metallic iron. If \*1.12 (1.1176) gms. of the liquor are taken, as the U. S. P. directs, each cc. of the V. S. used represents 0.5% of metallic iron.

**Iron and Ammonium Citrate** (Ferri et Ammonii Citras).—The precise chemical constitution of this preparation is not determined. Therefore the metallic iron only is estimated, of which it should contain 16 per cent.

**Ammonio-ferric Tartrate** (Ferri et Ammonii Tartras).—The exact chemical composition of this compound is not known. It is, theoretically,  $2(\text{FeO})\cdot\text{NH}_4\text{C}_4\text{H}_4\text{O}_6\cdot 3\text{H}_2\text{O}$ . It should contain 17 per cent. of metallic iron.

**Potassio-ferric Tartrate** (Ferri et Potassii Tartras).—There is some difference of opinion as to the composition of this salt. It is probably a double salt, consisting of one molecule of ferric tartrate,  $\text{Fe}_2(\text{C}_4\text{H}_4\text{O}_6)_3$ , and one of potassium tartrate,  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ , with one of  $\text{H}_2\text{O}$ . It should contain 15 per cent. of metallic iron.

**Soluble Ferric Phosphate** (Ferri Phosphas Solubilis).—This salt is called soluble ferric phosphate in order to distinguish it from the true ferric phosphate. It is not a definite chemical compound, but a mixture



of citrate and phosphate of sodium and iron. It should contain 12 per cent of metallic iron.

The foregoing four salts being of indefinite chemical composition, are tested for metallic iron only, as follows :

0.56 (0.5588) gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of 100 cc.) in 15 cc. of water and 2 cc. of hydrochloric acid. 1 gm. of potassium iodide is then added, and the mixture kept at 40° C. (104° F.) for half an hour, then cooled, a few drops of starch T. S. added, and decinormal sodium thiosulphate V. S. delivered in slowly from a burette until the blue or greenish color of the liquid is completely discharged. Each cc. of  $\frac{N}{10}$  V. S. represents 1 per cent. of metallic iron, if 0.56 (0.5588) gm. of the salt is taken.

**Iron and Quinine Citrate** (Ferri et Quininæ Citras).—The U. S. P. gives an assay process for quinine and one for iron to be applied to this salt.

#### ESTIMATION OF THE QUININE.

1.12 (1.1176) gms. of the salt are dissolved in a capsule in 20 cc. of water, with the aid of gentle heat.

The solution is poured into a separator, the capsule is rinsed with a little water, and the rinsings added to the liquid in the separator; when this has become cool, add 5 cc. of ammonia water and 10 cc. of chloroform, and shake. Allow the liquids to separate, draw off the chloroformic layer, and add to the residual liquid a second and a third portion of 10 cc. of chloroform added, shaking after each addition, and drawing off the chloroformic solution. The combined chloroformic



solutions are evaporated spontaneously in a tared capsule, and the residue dried at 100° C. (212° F.) to a constant weight. It should weigh not less than 0.1288 gm.

$$\frac{0.1288 \times 100}{1.1176} = 11.5\% \text{ of dried quinine.}$$

In the above assay the ammonia water precipitates the quinine and the chloroform dissolves it. Then by evaporating the chloroformic solution the quinine is obtained.

#### ESTIMATION OF THE IRON.

The aqueous liquid from which the quinine has been removed, as above described, is heated on a water-bath until the odor of chloroform and ammonia has disappeared; allow the liquid to cool, and dilute it with water to the volume of 50 cc. Take 25 cc. of this, put it in a glass-stoppered bottle (having a capacity of 100 cc.), add 2 cc. of hydrochloric acid and 1 gm. of potassium iodide, and digest at 40° C. (104° F.) for half an hour. Allow it to cool, add a few drops of starch T. S. and titrate with decinormal sodium thiosulphate V. S. until the blue or greenish color is discharged.

Each cc. of the volumetric solution represents 0.0056 (0.005588) gm. of metallic iron, or 1 per cent. 14.5 cc. should be required.

$$\begin{aligned} 0.0056 \times 14.5 &= 0.0812 \text{ gm.} \\ \frac{0.0812 \times 100}{0.56} &= 14.5\% \end{aligned}$$

**Soluble Citrate of Iron and Quinine (Ferri et Quininæ Citras Solubilis).—**This salt is assayed for

quinine and iron in the manner above described under *Ferri et Quininæ Citras*, and should respond to the requirements for the latter.

**Iron and Strychnine Citrate** (*Ferri et Strychninæ Citras*).—This salt should be tested quantitatively for strychnine and iron.

#### ESTIMATION OF THE STRYCHNINE.

\*2.24 (2.2352) gms. of the salt are dissolved in a separator in 15 cc. of water, 5 cc. of ammonia water are then added and 10 cc. of chloroform, and the mixture shaken. Set aside so as to allow the liquids to separate, draw off the chloroformic layer, add a second and a third portion of 10 cc. of chloroform, shaking each time and drawing off the chloroformic solution. The chloroformic extracts are then mixed, and allowed to evaporate spontaneously in a tared capsule. The residue is then dried at 100° C. (212° F.) to a constant weight.

This residue should not weigh less than 0.02 gm. nor more than 0.0224 gm., corresponding to not less than 0.9 nor more than 1 per cent. of strychnine.

$$\frac{.0224 \times 100}{2.24} = 1\%$$

#### ESTIMATION OF THE IRON.

The aqueous liquid from which the strychnine has been removed in the manner described above, is heated on a water-bath until the chloroform and ammonia are entirely volatilized. This is then allowed to cool, and diluted with water to the volume of 100 cc. 25 cc. of

this are transferred to a glass-stoppered bottle (having a capacity of 100 cc.), 2 gms. of hydrochloric acid and 1 gm. of potassium iodide are then added, and the mixture kept at a temperature of 40° C. (104° F.) for half an hour. After it has been allowed to cool add a few drops of starch T. S., and titrate with decinormal sodium thiosulphate V. S. until the blue or greenish color of the liquid is entirely discharged. 16 cc. of the  $\frac{N}{10}$  V. S. should be required to produce this result, each cc. corresponding to 1 per cent. or 0.0056 gm. of metallic iron.

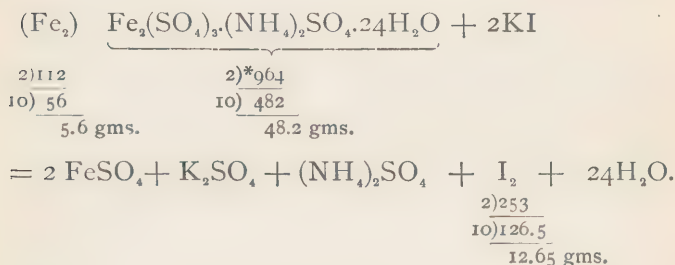
$$\begin{aligned} 0.0056 \times 16 &= 0.0896 \text{ gm.} \\ \frac{0.0896 \times 100}{0.56} &= 16\% \text{ of Fe.} \end{aligned}$$

**Ammonio-ferric Sulphate** (Ferri et Ammonii Sulphas; Ammonio-ferric Alum),  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 + 24\text{H}_2\text{O} = \left\{ \begin{array}{l} 962.1 \\ *964 \end{array} \right.$ .—This salt has a definite chemical composition, and therefore by determining the quantity of metallic iron the quantity of pure salt may be found by calculation.

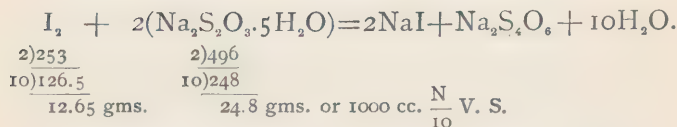
The U. S. P. process for assay is as follows:

0.56 (0.5588) gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of 100 cc.) in 15 cc. of water and 2 cc. of hydrochloric acid, 1 gm. of potassium iodide is then added, and the mixture kept at a temperature of 40° C. (104° F.) for half an hour. It is then allowed to cool, and mixed with a few drops of starch T. S., and titrated with decinormal sodium thiosulphate V. S. until the blue or greenish color of the

liquid is discharged. Not less than 11.6 cc. of the  $\frac{N}{10}$  V. S. should be required, each cc. corresponding to 1 per cent, or .0056 gm. of metallic iron, or 0.0482 gm. of the salt. See the following equations:



Then



Thus it is seen that 1 cc. of  $\frac{N}{10}$  V. S. represents 0.01265 gm. of iodine, and this corresponds to 0.0482 gm. of ammonio-ferric sulphate, or 0.0056 gm. of metallic iron.

$$0.0482 \times 11.6 = 0.55912 \text{ gm.}$$

$$\frac{0.55912 \times 100}{11.6} = 99.8\% \text{ of the pure salt.}$$

$$0.0056 \times 11.6 = .06496 \text{ gm.}$$

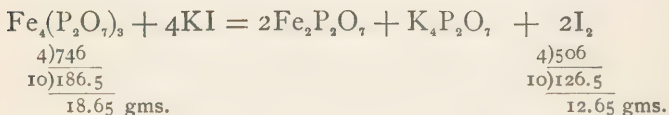
$$\frac{.06496 \times 100}{0.56} = 11.6\% \text{ of Fe.}$$

**Soluble Ferric Pyrophosphate** (Ferri Pyrophosphas Solubilis).—This is estimated according to the U. S. P. in the following manner:

0.56 (0.5588) gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of 100 cc.) in 10 cc of water, then 10 cc. of hydrochloric acid and subsequently 40 cc. of water are added. Then 1 gm. of potassium iodide is put into the solution and the temperature kept at 40° C. (104° F.) for half an hour. The liquid is then cooled and a few drops of starch T. S. added, and the  $\frac{N}{10}$  sodium thiosulphate V. S. delivered in from a burette, until the blue or greenish color is completely discharged. Each cc. of the  $\frac{N}{10}$  V. S. represents 1 per cent. or 0.0056 gm. of metallic iron.

True ferric pyrophosphate has the chemical composition  $\text{Fe}_4(\text{P}_2\text{O}_7)_3 + 9\text{H}_2\text{O}$ . The soluble ferric pyrophosphate of the U. S. P. is a mixture of ferric pyrophosphate and sodium citrate.

The reaction with potassium iodide is expressed as follows:



Thus 18.65 gms. of ferric pyrophosphate cause the liberation of 12.65 gms. of iodine, and since each cc. of  $\frac{N}{10}$  sodium thiosulphate V. S. will absorb, and consequently represent, .01265 gm. of iodine, it corresponds to 0.01865 gm. of pure ferric pyrophosphate.

10 cc. of the decinormal solution is the quantity which the U. S. P. requires should be used.

$$0.01865 \times 10 = 0.1865 \text{ gm.}$$

$$\frac{0.1865 \times 100}{0.56} = 33.3\%$$

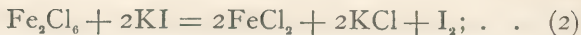
of ferric pyrophosphate, which corresponds to 10% of metallic iron in the U. S. P. salt.

**Ferric Valerianate** (Ferri Valerianas),  $\text{Fe}_2(\text{C}_5\text{H}_9\text{O}_2)_6$ , = {\*718.—The true ferric valerianate is illustrated by the above formula, but the U. S. P. salt is of variable composition, and should contain not less than 15%, nor more than 20%, of iron in combination.

The estimation is conducted as follows: \*0.56(0.5588) gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of 100 cc.) in 2 cc. of hydrochloric acid. This decomposes the salt, forming ferric chloride and liberating valerianic acid. 15 cc. of water are now added, together with 1 gm. of potassium iodide, and the mixture heated to  $40^\circ \text{C}$  ( $104^\circ \text{F.}$ ) and kept at that temperature for half an hour; it is then cooled, and the liberated iodine estimated with decinormal sodium thiosulphate V. S., using starch T. S. as indicator.

Not less than 15 cc. nor more than 20 cc. of the  $\frac{\text{N}}{10}$  V. S. should be required to discharge the color of starch iodide. Each cc. corresponds to 1% of metallic iron. The reactions are expressed by the following equations:





**Liquor Ferri Acetatis** (Solution of Ferric Acetate).

—This is an aqueous solution, containing about 31% of anhydrous ferric acetate  $(\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_6 = \left\{ \begin{array}{l} *464.92 \\ 466 \end{array} \right.$ , corresponding to 7.5% of iron. 1.12 (1.1176) gms. of the solution are introduced into a glass-stoppered bottle (having a capacity of 100 cc.), together with 15 cc. of water and 2 cc. of hydrochloric acid.

1 gm. of potassium iodide is then added and the mixture kept at a temperature of 40° C. (104° F.) for half an hour; then cooled, and, after adding a few drops of starch T. S., pass into it from a burette decinormal sodium thiosulphate V. S. until the blue or greenish color of the liquid has completely disappeared.

Each cc. of the decinormal solution thus consumed represents 0.5% of metallic iron.

If 0.56 (0.5588) gm. of the solution is used instead of 1.12 (1.1176) gm., and treated as described above, each cc. of the  $\frac{N}{10}$  V. S. represents 1% of metallic iron, or 0.0056 gm.

The principal reaction is expressed by the following equation:



$$\begin{array}{r} 2)464.92 \\ 10)232.46 \\ \hline 23.246 \text{ gms.} \end{array}$$

$$\begin{array}{r} 2)253 \\ 10)126.5 \\ \hline 12.65 \text{ gms.} \end{array}$$



Thus each cc. of the  $\frac{N}{10}$  V. S. also represents 0.023246 gm. of ferric acetate.

15 cc. of the  $\frac{N}{10}$  V. S. should be required if 1.12 gms. of solution are taken.

$$0.023246 \times 15 = 0.34869 \text{ gm.}$$

$$\frac{0.34869 \times 100}{1.12} = 31.1\% \text{ of ferric acetate.}$$

7.5 cc. the  $\frac{N}{10}$  V. S. should be consumed if 0.56 gm. is taken.

$$0.023246 \times 7.5 = 0.17434 \text{ gm.}$$

$$\frac{0.17434 \times 100}{0.56} = 31.1\%$$

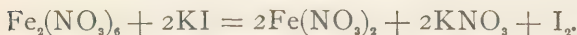
### **Liquor Ferri Nitratis** (Solution of Ferric Nitrate).

—An aqueous solution containing about 6.2% of anhydrous ferric nitrate  $(\text{Fe}_2(\text{NO}_3)_6 = \left\{ \begin{smallmatrix} 483.1 \\ *484 \end{smallmatrix} \right.$ , and corresponding to about 1.4% of metallic iron.

Introduce into a glass-stoppered bottle (having a capacity of 100 cc.) 1.12 (1.1176) gms. of the solution, together with 15 cc. of water and 2 cc. of hydrochloric acid. Then add to the mixture 1 gm. of potassium iodide, and keep it at a temperature of 40° C. (104° F.) for half an hour. Allow the mixture to cool, and estimate the liberated iodine with decinormal sodium thio-sulphate V. S., using starch T. S. as indicator. When the blue or greenish color of starch iodide has entirely disappeared, the reaction is completed.

2.8 cc. of the  $\frac{N}{10}$  V. S. should be required, each cc. corresponding to 0.5% of metallic iron.

The reaction between the ferric nitrate and potassium iodide is as follows:



$$\begin{array}{r} 2)483.1 \\ 10)241.5 \\ \hline 24.15 \text{ gms.} \end{array}$$

$$\begin{array}{r} 2)253 \\ 10)126.5 \\ \hline 12.65 \text{ gms.} \end{array}$$

or 1000 cc.  $\frac{N}{10}$  V. S.

Thus each cc. of the decinormal sodium thiosulphate V. S. represents 0.02415 gm. of ferric nitrate.

**Liquor Ferri Subsulphatis** (Solution of Basic Ferric Sulphate; Monsel's Solution).—An aqueous solution of basic ferric sulphate of variable composition, chemically corresponding to about 13.6% of metallic iron.

1.12 (1.117) gms. of the solution are introduced into a flask (having a capacity of 100 cc.), together with 15 cc. of water and 2 cc. of hydrochloric acid. 1 gm. of potassium iodide is then added and the mixture digested for half an hour at a temperature of 40° C. (104° F.). It is then cooled, and after adding a few drops of starch T. S., it is titrated with decinormal sodium thiosulphate V. S. When the blue or greenish color of the liquid disappears, the reaction is completed. 27.2 cc. should be required to complete the reaction, each cc. corresponding to 0.5% or 0.0056 gm. of metallic iron.

$$0.0056 \times 27.2 = 0.15232 \text{ gm.}$$

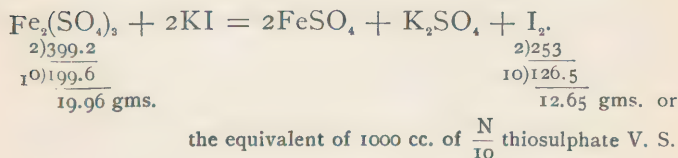
$$\frac{0.15232 \times 100}{1.12} = 13.6\%$$

**Liquor Ferri Tersulphatis** (Solution of Ferric Sulphate).—An aqueous solution of normal ferric sulphate  $(\text{Fe}_2(\text{SO}_4)_3 = \left\{ \begin{smallmatrix} 399.2 \\ *400 \end{smallmatrix} \right\})$  containing about 28.7 per cent. of the salt, and corresponding to about 8 per cent. of metallic iron.

1.12 (1.1176) gms. of the solution are introduced into a 100-cc. glass-stoppered bottle, together with 15 cc. of water and 2 cc. of hydrochloric acid; 1 gm. of potassium iodide is then added, and the mixture kept at a temperature of  $40^\circ \text{C}$ . ( $104^\circ \text{F}$ .) for half an hour, then allowed to cool, and the liberated iodine estimated in the usual way with  $\frac{\text{N}}{10}$  sodium thiosulphate V. S., using starch T. S. as indicator.

About 16 cc. of the  $\frac{\text{N}}{10}$  V. S. should be required.

The following equation illustrates the reaction :



Thus each cc. represents 0.01996 gm. of ferric sulphate, which corresponds to 0.5 per cent. or 0.0056 gm. of metallic iron.

If 16 cc. are used, the solution of ferric sulphate contains  $0.01996 \times 16 = 0.31936$  gm.

$$\frac{0.31936 \times 100}{1.12} = 28.5\%$$

of pure ferric sulphate, and

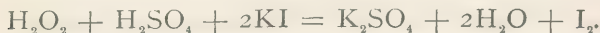
$$0.0056 \times 16 = 0.0896 \text{ gm.},$$

$$\frac{.0896 \times 100}{1.12} = 8\%$$

of metallic iron.

**Hydrogen Peroxide**,  $\text{H}_2\text{O}_2 = \left\{ \begin{array}{l} 33.92 \\ 34 \end{array} \right.$ .—The iodometric method, which originated with Kingzett, is based upon the fact that iodine is liberated from potassium iodide by hydrogen peroxide, in the presence of sulphuric acid, and that this liberation of iodine is in direct proportion to the available oxygen contained in the peroxide.

Then by determining the amount of iodine liberated, the available oxygen is readily found.



$$\frac{2)34}{17} = 1 \text{ available O} = \frac{2)16}{8}$$

$$\frac{2)253}{126.5}$$

This shows that 126.5 gms. of iodine are liberated by 17 gms. of absolute peroxide, which are equivalent to 8 gms. of available oxygen.

Thus 1000 cc. of  $\frac{\text{N}}{10}$  sodium thiosulphate V. S., which absorb and consequently represent 12.65 gms. of iodine, are equivalent to 1.7 gms. of  $\text{H}_2\text{O}_2$  or 0.8 gm. of available oxygen.

Each cc. of this  $\frac{\text{N}}{10}$  V. S., then, represents, of  $\text{H}_2\text{O}_2$  \*0.0017 gm., of available oxygen \*0.0008 gm.

The coefficients for weight of  $\text{H}_2\text{O}_2$  and of oxygen, it is seen, are identical with those used in the permanganate process. Therefore the coefficient for volume is also the same in this method as in the other, namely, 0.5594.

The process is carried out as follows: Take 2 or 3 cc. of sulphuric acid, dilute it with about 30 cc. of water, add an excess of potassium iodide (about 1 gm.), and then 1 cc. of hydrogen peroxide. After the mixture has been allowed to stand five minutes starch T. S. is added, and the titration with  $\frac{N}{10}$  sodium thiosulphate begun.

Note the number of cc. required to discharge the blue color, and multiply this number: by 0.0017 gm. to find the quantity, by weight, of  $H_2O_2$ ; by 0.0008 gm. to find the weight of available oxygen; by 0.5594 cc. to find the volume of available oxygen.

If 18 cc. are required, the solution is of  $0.5594 \times 18 = 10.0683$  volume strength.

$$0.0017 \times 18 = .0306 \text{ or } 3.06\% H_2O_2.$$

$$0.0008 \times 18 = .0144 \text{ or } 1.44\% \text{ of oxygen.}$$

With this method the author has always obtained satisfactory results. The lack of uniformity in the reaction, which is frequently reported, is doubtless due to the use of insufficient acid.

TABLE OF SUBSTANCES, ESTIMATED BY DECINORMAL SODIUM THIOSULPHATE V. S.

Name.	Formula.	Molecular Weight.	Factors.
			Gm.
Chlorine .....	$Cl_2$	70.68	.003537
Ferric acetate .....	$Fe_2(C_2H_3O_2)_6$	464.92	.023446
Ferric chloride .....	$Fe_2Cl_6 + 12H_2O$	539.5	.026975
Ferric citrate .....	$Fe_2(C_6H_5O_7)_2$	488.48	.024424
Ferric nitrate .....	$Fe_2(NO_3)_6$	483.1	.02415
Ferric phosphate .....	$Fe_2(PO_4)_2$	*302	.0151
Ferric pyrophosphate.....	$Fe_4(P_2O_7)_3$ anhydrous	*746	.01865
Ferric sulphate .....	$Fe_2(SO_4)_3$	399.2	.01996
Ferric and ammonium sulphate.	$Fe_2(NH_4)_2(SO_4)_4 + 24H_2O$	*904.0	.0482
Ferric valerianate .....	$Fe_2(C_5H_9O_2)_6$	*718	.0359
Hydrogen peroxide .....	$H_2O_2$	33.92	.001696
Iodine .....	$I_2$	253	.01265
Iron, in ferric salts .....	$Fe_2$	111.76	.005588
Oxygen, available, weight. ....	$O_2$	*32	.0008
Oxygen, available volume .....	$O_2$	*32	.5594 cc.

## PART II.

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### CHAPTER XIV.

#### SANITARY ANALYSIS OF WATER.

IN collecting samples of water great care must be exercised in order to secure a fair representation of the water and to avoid the introduction of foreign matters.

The samples should be collected in clean glass-stoppered bottles having a capacity of from 2 to 5 pints.

It is well to completely fill the bottle with water, then empty it, and again fill with the water to be analyzed.

In taking samples from lakes, reservoirs, or slow streams the bottle should be submerged, so as to avoid collecting any water that has been in direct contact with the air.

In collecting from pump-wells a few gallons should be pumped out before taking the sample in order to remove that which has been standing in the pump.

If the public water-supply is to be analyzed, take the water from a hydrant communicating directly with the street main, and not from a cistern.

At the time of collecting, a record should be made of those surroundings and conditions which might influ-

ence the character of the water, such as proximity of cesspools, sewers, stables, and factories.

It should also be noted whether the sample is from a deep or shallow well, a river, spring, or artesian well.

The nature of the soil and the different strata of the locality must also be taken into account.

The sample should be kept in the dark and analyzed with as little delay as possible.

**Color.**—This may be taken by looking down through a column of water in a colorless glass tube about two feet long, standing upon a piece of white paper.

A comparison is made with a second tube containing distilled water.

Another way of determining the color is by the use of a colorless glass tube two feet long and two inches in diameter, closed at each end, with disks of colorless glass cemented on, but having a small opening at one end for filling and emptying the tube.

To use this tube, it is half filled with the water to be examined and placed in a horizontal position. A piece of white paper is held at one end of the tube, and then by looking through from the other end the color of the liquid is observed, and a comparison of tint made between the lower half of the tube containing the water and the upper half containing air.

**Odor.**—Three or four ounces of water are placed in a small flask fitted with a cork through which is passed a thermometer; the flask is placed in a water-bath and heated to 100° F. The flask is then shaken, the cork withdrawn, and the odor immediately observed.

In this way, satisfactory and uniform tests are obtained, and a practised nose can frequently detect pollution.



**Reaction.**—This may be determined by the use of a neutral solution of litmus. If an acid reaction is obtained, the water should be boiled in order to determine if it is due to carbonic acid; if the red color disappears upon boiling, the acid reaction is due to carbonic acid.

Phenolphthalein or lacmoid may also be used for this purpose.

**Suspended Matter.**—A litre of the turbid water is passed through a dried and weighed filter. The filter is then again dried and weighed, and the increase in weight represents the suspended matter in one litre of the water.

#### TOTAL SOLIDS.

A platinum dish having a capacity of about 120 cc. is heated to redness, then cooled under a desiccator, and weighed. 100 cc. of the water is then introduced and evaporated over a low-temperature burner at a moderate heat. When the residue appears dry the heat may be increased by placing the dish in an air oven kept at a temperature of about 212° F. until it ceases to lose weight; finally cool under a desiccator, and weigh. In waters of exceptional purity it may be advisable to use larger quantities, such as 250 cc.

The increase in weight of the dish represents approximately the total solids contained in the water taken.

If the solid residue does not exceed 57 parts per 100,000, no reason is afforded for rejecting the water for domestic use. It has been found that the figure for total solids obtained thus, does not truly represent the sum of the organic and mineral matters in all cases.

Experiments have been made with urea dissolved in

varying quantities of water. Where the solution contained 1 gm. of urea the residue after evaporation varied from 0.98 to 0.007 gm.

Besides the possible loss of organic matter during the evaporation, some of the mineral constituents may retain with great obstinacy, large quantities of water in the form of water of crystallization, which would cause an error in the opposite direction.

Thus the determination of total solids is only an approximation.

#### ORGANIC AND VOLATILE MATTER—LOSS ON IGNITION.

Though the mineral matter in a water must to some extent be taken into account in judging of a water, the organic matter is of far greater importance. The really injurious matters are more probably the organic.

It is therefore important to determine as near as possible their quantity and nature.

It was naturally supposed that by igniting the residue obtained from evaporation of the water, the organic matter would be burned out, and that the loss of weight would then represent the organic matter. But as waters ordinarily contain some earthy carbonates, which upon ignition are deprived of carbonic-acid gas and converted into oxides, it was customary to add a few drops of carbonic-acid water or ammonium carbonate to the ash, and then dry and weigh the residue.

Ignition, however, decomposes other salts which may be contained in water, and may even volatilize some wholly; therefore the loss on ignition cannot be truly called the organic matter. Hence the expressions "Organic and Volatile Matter," and "Loss on Ignition."

Frankland recommends ignition as a rough qualita-

tive test for the presence of organic matter, the degree of blackening which takes place, giving some idea of the probable amounts of organic matter present.

### CHLORINE

may be estimated by the use of decinormal or centinormal silver-nitrate solution; but analysts generally use a solution of such strength that 1 cc. will represent 0.001 gm. of chlorine.

*Standard Silver-nitrate Solution.*—Dissolve 4.794 gms. of pure recrystallized silver nitrate in sufficient water to make 1000 cc.

*Potassium-chromate Solution.*—Five gms. of neutral potassium chromate are dissolved in 100 cc. of water and a weak solution of silver nitrate added, drop by drop, until a slight permanent red precipitate is produced, which is allowed to settle in the bottle, or separated by filtration.

*The Process.*—Measure out 100 cc. of the water to be analyzed into a beaker or white basin; add a few drops of the potassium-chromate solution; then run in slowly from a burette, the silver-nitrate solution until a slight red tint appears. Note the number of cc. of silver solution used. Each cc. represents 0.001 gm. (1 milligramme). If the chlorine is present in small quantity, about 250 cc. of the water should be evaporated to about one fifth before titrating with the silver-nitrate solution.

*Example.*—100 cc. of water taken, 4 cc. of silver solution consumed; thus showing that the 100 cc. of water contained 0.004 gm. of chlorine, or 100,000 cc. contained 4 gms.

Multiplied by 10 gives parts per million.

The water must be perfectly neutral before titration. If acid, it must be shaken with a little pure precipitated calcium carbonate.

#### AMMONIA.

When organic matter decomposes spontaneously, it first forms ammonia, then nitrites, and finally nitrates. Thus the presence of ammonia in water is generally conceded to indicate decomposing organic matter, and hence its determination is an important part of the sanitary examination of water.

The ammonia is generally spoken of as free ammonia and albuminoid ammonia, or, more properly, as ammonium salts and ammonia from organic nitrogen.

The sanitary examination of a water should always include a quantitative determination of nitrogen in both compounds.

The process requires several solutions and considerable care in manipulation. The solutions required are :

1. *Nessler's Solution*, made by dissolving 35 gms. of potassium iodide in 100 cc. of water and 17 gms. of mercuric chloride in 300 cc. of water. The liquids may be heated to aid solution, but if so, must be again cooled. When solution is complete, add the latter to the former until a permanent precipitate is produced; then dilute with a 20% solution of sodium hydroxide to 1000 cc. Now add mercuric-chloride solution again until a permanent precipitate is formed. Let the mixture stand until settled, then decant off the clear solution for use. The bulk of the solution should be kept in a well-stoppered bottle, and a small quantity transferred from time to time to a small bottle, from which it should be used. This solution

improves on keeping, and reacts with extremely minute quantities of ammonia.

2. *Sodium-carbonate Solution*.—A 20% solution of pure freshly-ignited sodium carbonate in water free from ammonia.

3. *Standard Ammonium-chloride Solution*.—Dissolve 0.3138 (\*.314) gm. of pure ammonium chloride in water to 100 cc. For use dilute 1 cc. of this solution with 99 cc. of distilled water free from ammonia. Each cc. of this solution contains 0.00001 gm. of ammonia.

4. *Alkaline Potassium-permanganate Solution*.—Dissolve 200 gms. of pure potassium hydroxide and 8 gms. of pure potassium permanganate in sufficient ammonia-free water to make 1000 cc.

5. *Ammonia-free Water*.—If the distilled water of the laboratory gives a reaction with Nessler's solution, it should be treated with sodium carbonate, about 1 gm. to the litre, and boiled until one fourth has been evaporated.

A good clear hydrant water when treated with sodium carbonate and distilled yields ammonia-free water. The first portion which comes over has of course some ammonia in it, and small portions of the distillate should be tested with Nessler's reagent until no more reaction is obtained; the remainder, except the very last portion, should be collected.

Ammonia-free water may also be obtained by distilling water acidulated with sulphuric acid. In the first two processes the ammonia is converted into a volatile salt and is easily dissipated, or appears in the first distillate; in the last process it is converted into a non-volatile salt, which does not distil over.

**Apparatus Required.**—A still, consisting of a glass

retort, having a capacity of about 700 cc., which is connected with a Liebig's condenser by an air-tight joint.

The heat is applied by means of a low-temperature burner, the iron ring of which is removed, so that the retort rests directly upon the gauze. (See Fig. 25.)

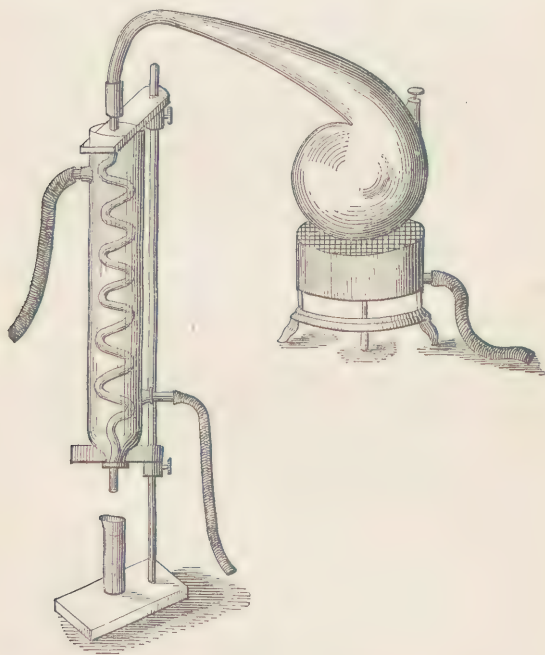


FIG. 25.

*Cylinders for Comparative-color Tests.*--These cylinders are made of pure colorless glass, about one inch in diameter, having a capacity of about 100 cc. and graduated at 50 cc. These should either have a milk-glass foot, or should stand upon white paper. Two or more of these are required.



*The Process.*—The retort and condenser are thoroughly rinsed out with ammonia-free water. Then 500 cc. of the water to be tested are introduced, and about 5 cc. of sodium-carbonate solution added to make the water alkaline. The water is then gently boiled until 50 cc. of distillate are obtained. This distillate is transferred to one of the color-comparison cylinders and 2 cc. of Nessler's reagent added; a yellow color is produced, which develops more fully in 3 or 5 minutes, and the intensity of which is proportionate to the amount of ammonia present.

The color produced is exactly matched by introducing into another cylinder 50 cc. of ammonia-free water and an accurately measured quantity of the standard ammonium-chloride solution, and 2 cc. of Nessler's reagent, as before.

According as the color so produced is deeper or lighter than that obtained from the water, other solutions are prepared for comparison, containing smaller or larger proportions of the ammonium chloride, until the proper color is produced.

The distillation is continued, and successive portions of 50 cc. of the distillate taken and tested, until the liquid no longer reacts with Nessler's reagent. The sum of the figures obtained from the several distillates gives the total ammonia, existing in ammonium compounds, in the 500 cc. of water taken.

The residue in the retort serves for the determination of the nitrogen of the organic matter, which is converted by the alkaline permanganate into ammonia (*albuminoid ammonia*).

50 cc. of the alkaline permanganate are placed in a porcelain dish of about 150 cc. capacity, the dish nearly



filled with distilled water, and then the liquid boiled down to 50 cc.

This is added to the residue in the retort, the distillation resumed, and the ammonia estimated in each 50 cc. of the distillate, as before described.

It is the practice of some analysts to mix the distillates of each of the above operations, and thus make determinations merely of the total quantity of ammonia and albuminoid ammonia. By so doing valuable information may be lost, since it has been pointed out that the ammonia may be differently distributed in the distillates, according to the state, decomposing or otherwise, in which the ammonia exists in the water. If the ammonia distils over very rapidly, it indicates that the organic matter is in a putrescent or decomposing condition.

If, on the other hand, it distils gradually, it indicates the presence of organic matter in a comparatively stable or fresh condition. It is best, therefore, to keep the record of each distillate, so that the rapidity with which the ammonia is set free, as well as the actual amount, may be known.

The greatest care should be exercised in order to avoid the introduction of ammonia in any way during the course of the analysis, since small quantities of ammonia compounds and nitrogenous matters are everywhere present. All measuring-vessels, cylinders, etc., should be thoroughly rinsed before using.

#### NITROGEN AS NITRATES.

**Solutions Required.**—*Acid Phenyl Sulphate*.—18.5 cc. of strong sulphuric acid are added to 1.5 cc. of



is compared to that given by the water; and one or the other of the two solutions diluted until the tints agree.

The comparative volumes of the liquids furnish the necessary data for determining the amount of nitrate present, as the following example will show. Five cc. of the standard nitrate are treated as above, and made up to 100 cc. Each cc. represents 0.0001 gm. of nitrogen.

$$\begin{array}{r}
 .0001 \\
 5 \\
 \hline
 .0005 \text{ gm. N per 100 cc.} \\
 10 \\
 \hline
 .0050 \text{ gm. N per 1000 cc.}
 \end{array}$$

Suppose 100 cc. of water similarly treated are found to require dilution to 150 cc. before the tint will match that of the standard; then

$$100 : 150 :: .005 : x. \quad x = 0.0075.$$

That is, the water contains 7.5 milligrams of nitrogen as nitrate per litre.

Care should be taken that the same quantity of acid phenyl sulphate is used for the water and for the comparison liquid, otherwise different tints instead of depths of tints are produced.

With river or spring waters 25 to 100 cc. should be evaporated for the test, but with subsoil and other waters which probably contain much nitrates 10 cc. will be sufficient.

*The Copper-zinc Process.*—500 cc. of the water are acidulated with oxalic acid, and half of this is poured into each of two wide-mouthed bottles. Into one of these is put a copper-zinc couple, made by taking a piece of sheet zinc ( $4 \times 6$  in.) and rolling it into a loose coil and immersing it in a 1.5-per-cent. solution of copper sulphate until the surface is covered with an even layer of copper.

Cork both bottles and let stand 24 hours. Remove 50 cc. from each bottle and Nesslerize as directed under Ammonia.

The difference between the two readings gives the ammonia due to the reduction of the nitrates and nitrites present. The nitrogen in the nitrites, which is separately determined, must be subtracted, when the remaining nitrogen will be that from the nitrates.

#### NITROGEN AS NITRITES.

**Solutions Required.**—1. *Naphthylammonium Chloride* (*Naphthalamine Hydrochlorate*).—Saturated solution in water free from nitrites. It should be colorless (0.5 gm. dissolved in 100 cc. of boiling water). This solution should be kept in a glass-stoppered bottle with a little animal charcoal, which will keep the solution colorless.

2. *Sulphanilic Acid* (*Para-amido-benzene—Sulphonic Acid*).—A saturated solution in water free from nitrites (1 gm. in 100 cc. of hot water).

*Hydrochloric Acid.*—25 cc. of concentrated pure hydrochloric acid mixed with 75 cc. of water free from nitrites.

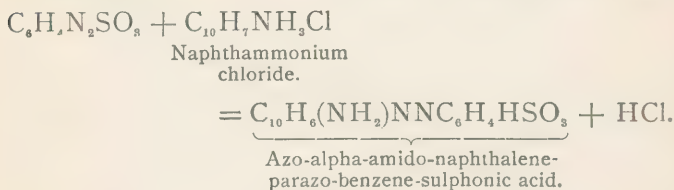
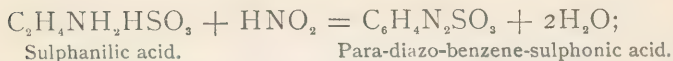
*Standard Sodium Nitrite.*—0.275 gm. pure silver nitrite is dissolved in pure water, and a dilute solution of pure sodium chloride added until a precipitate ceases to form. It is then diluted with pure water to 250 cc. and allowed to stand until clear. For use 10 cc. of this solution are diluted to 100 cc. It must be kept dark. One cc. of the dilute solution is equivalent to .00001 gm. of nitrogen.

A standard solution of silver nitrite is used by some chemists, but the above is said to give better results.

*The Process.*—100 cc. of the water is placed in one of the color-comparison cylinders, the measuring-vessels and cylinder having previously been rinsed with the water to be tested. By means of a pipette introduce into the water 1 cc. each of the solutions of sulphanilic acid, dilute hydrochloric acid, and naphthylammonium-chloride solution in the order named. It is convenient to have three pipettes—one for each of these solutions, and to use them for no other purpose. In all cases the pipettes should be rinsed with ammonia-free water before using them. Into another clean comparison-cylinder introduce 1 cc. of the standard nitrite solution and make up to 100 cc. with pure water; then add the same reagents as were added to the water in the other cylinder.

A pink color is produced in the presence of nitrites, which requires in dilute solutions half an hour for complete development. At the end of that time the darker solution is diluted with water until the tints are matched, and the calculation made as explained under nitrates.

The reactions are explained by the following equations:



The last-named body gives the color to the liquid.

*Example.*—Suppose that 100 cc. of the water require dilution to 125 cc. in order to bring it to the same tint as that produced by 1 cc. of the standard nitrite solution, which contains .00001 gm. of nitrogen as nitrite.

$$100 : 125 :: .00001 : x. \quad 0.0000125 \text{ gm. in } 100.$$

That is, 100 cc. of water contain 0.0000125 gm. of N ;  
0.0125 gm. in 100,000 cc.

#### OXYGEN-CONSUMING POWER.

Potassium permanganate readily yields up its oxygen, especially in the presence of a strong mineral acid, as sulphuric. It oxidizes many salts, and organic matter.

This property led to the idea that this salt may be used for burning up (chemically speaking) the organic matter in water, and that the quantity of permanganate used could be relied upon as a means of measuring the organic matter in water.

This method does not distinguish between animal and vegetable matter, nor does the quantity of

permanganate consumed represent only the organic matter.

The organic matters in water are very variable in character and condition, and their oxidability is subject to much difference.

Nevertheless as a high oxygen-consuming power certainly indicates pollution by organic matter, the process is of considerable value.

The following is a convenient method for approximating the oxygen-consuming power of a water:

**Solutions Required.**—*Potassium Permanganate.*—0.395 gm. of pure potassium permanganate is dissolved in distilled water, and the solution made up to 1000 cc. 1 cc. of this solution will yield under favorable circumstances 0.0001 gm. of oxygen.

*Diluted Sulphuric Acid.*—50 cc. of pure sulphuric acid are mixed with 100 cc. of water, and then just sufficient of the permanganate solution added to give the mixture a faint pink color, which remains after standing in a warm place four hours.

*The Process.*—Five stoppered bottles having a capacity of 500 cc. are thoroughly cleansed with strong sulphuric acid and then carefully rinsed with pure water, and 250 cc. of the water to be tested put into each one. 10 cc. of the dilute sulphuric acid is then added to each, together with regularly increasing quantities of the standard permanganate, say 2, 4, 6, 8, and 10 cc., respectively.

At the end of an hour they should be examined, to see which, if any, are decolorized. At the end of the fourth hour they should again be examined, and again at the expiration of twenty-four hours.

If all of the bottles are decolorized at or before the



fourth hour an additional 10 cc. of the permanganate solution should be added to each bottle.

With ordinary waters the first and probably the second bottle will be decolorized, while a little color will remain in the third, and the color in the fourth and fifth will be but little diminished. In this way an approximate figure for the oxygen-consuming power of the water may be obtained, which in most cases is all that is necessary. If a closer figure is desired, the experiment may be repeated, using quantities of permanganate intermediate between those marking the limits of the reaction.

Thus if the second bottle is decolorized and a faint color still remains in the third, repeat the experiment with 5 cc. of the permanganate.

This method of procedure has an advantage over some of the other processes, because the rate of oxidation can easily be seen. This is considered by some to be of more importance than the actual amount of oxygen consumed.

It must be remembered that nitrites, ferrous salts, sulphides, etc., consume oxygen as well as organic matter. It is therefore important to boil water containing hydrogen sulphide in order to drive the latter off. Nitrites may be removed by treating the water with sulphuric acid, and boiling. The nitrite is thus converted into nitrous acid, which is driven off by the heat. Or the oxygen required to convert the nitrites present into nitrates may be deducted from the total amount of oxygen consumed. 14 parts of nitrogen as nitrite require 16 parts of oxygen for oxidation into nitrate.

## PHOSPHATES.

**Solutions Required.**—*Ammonium Molybdate*.—Made by dissolving 10 gms. of molybdic anhydride in a mixture of 15 cc. of concentrated ammonia (sp. gr. .900) and 25 cc. of water. This solution is poured slowly, and with constant stirring, into a mixture of 65 cc. of concentrated nitric acid (sp. gr. 1.4) and 65 cc. of water, and allowed to stand until clear. It should be kept dark.

*The Process*.—One litre of the water is evaporated to about 50 cc.; a few drops of a dilute solution of ferric chloride are added, followed by a slight excess of ammonia. Ferric hydroxide is thus precipitated, which carries down with it all the phosphate. This precipitate is separated by filtration, dissolved on the filter in the smallest possible quantity of hot dilute nitric acid, and a little water passed through the filter. The filtrate and washings should not exceed 5 cc., and should, if more, be evaporated to this bulk.

The solution is now heated nearly to boiling and 2 cc. of the ammonium-molybdate solution added. If after half an hour an appreciable precipitate is formed, it is collected on a small weighed filter and its weight found after thorough drying. This weight, multiplied by 0.05 gives the amount of  $\text{PO}_4$ . If the quantity is too small to be collected and weighed in this manner, it is usually reported as "traces," "heavy traces," or "very heavy traces."

## HARDNESS.

The hardness of water, that is, its soap-destroying power, is due principally to the presence of calcium salts; but salts of magnesium, iron, and other metals may also contribute to this effect.

Two kinds of hardness are recognized :

1. "Temporary," which is due to the presence in water of the acid carbonates of calcium, magnesium, etc. By boiling, these salts are decomposed, the carbonic-acid gas being driven off, and the neutral carbonate formed, which is precipitated. Thus the water loses its hardness upon boiling.



2. "Permanent" hardness is due to the presence in water of salts of the above-mentioned metals which are not removed by boiling, such as the sulphates.

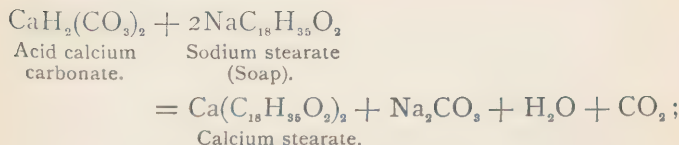
Hardness is estimated by means of a standard soap solution.

Many samples of water possess both temporary and permanent hardness, and it is sometimes desirable to estimate them separately.

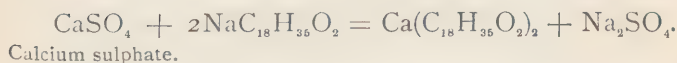
The total hardness is estimated in one sample, and the hardness in another sample is determined after boiling and filtering off the precipitated calcium carbonate.

The hardness found after boiling is the permanent hardness, and is the most objectionable form. The difference between the total and permanent hardness is the temporary hardness. To express the hardness in some tangible form, the usual custom in this country and in England is to give results in the corresponding amounts of calcium carbonate, i.e., practically to determine the amount of soap destroyed by a measured quantity of water, and then to state the results as the amount of calcium carbonate which would destroy that quantity of soap.

The reaction which takes place when soap is added to a hard water, is illustrated in the following equations:



or,



The calcium stearate, which is an insoluble calcium soap, is precipitated in both cases as a white curd-like mass.

The method for estimating hardness in water by the use of soap solution is known as Clark's method.

**Solutions Required.**—*Standard Soap Solution.*—Dissolve 10 gms. of shavings of air-dried Castile soap in a litre of dilute alcohol. Filter the solution if it is not clear, and keep it in a tightly-stoppered bottle.

*Standard Calcium Chloride Solution.*—Dissolve 1 gm. of pure calcium carbonate in the smallest excess of hydrochloric acid, then carefully neutralize with ammonia water, and add sufficient water to make up to one litre.

One cc. of this solution will contain the equivalent of 0.001 gm. of calcium carbonate. This solution is used for determining the strength of the soap solution, which is done as follows:

Measure out 10 cc. of this solution, add 90 cc. of distilled water, and run in the soap solution, drop by drop, from a burette until a lather is formed, which remains

for five minutes. Note the number of cc. of soap solution used.

We now repeat the experiment with 100 cc. of distilled water. The amount of the soap solution required to produce a permanent lather with the distilled water must be deducted from the amount used in the first test. Usually it will be about one half or one cc.

The 10 cc. of the calcium chloride solution contained the equivalent of 0.010 gm. of  $\text{CaCO}_3$ . Suppose in the above-mentioned test 8.5 cc. of the soap solution were used to produce a permanent lather, and 0.5 cc. were used by the distilled water. Then 8 cc. were used to precipitate 0.010 gm. of  $\text{CaCO}_3$ . Thus each cc. of this soap solution will represent  $\frac{1}{8}$  of .010 gm. = .00125 of calcium carbonate.

The soap solution may either be used as it is, or it may be diluted with dilute alcohol so that about 10.5 or 11 cc. of it will be required to produce a permanent lather with 10 cc. of the standard calcium chloride solution. If so diluted each cc. will represent 0.001 gm. of  $\text{CaCO}_3$ .

This is a convenient strength, because if 100 cc. of water are operated upon, each cc. of the soap solution used will represent 1 part of  $\text{CaCO}_3$  in 100,000 parts of water.

Measure 100 cc. of the water into a well-stoppered bottle having a capacity of about 250 or 300 cc. Add the soap solution gradually from a burette, one cc. at a time at first, and smaller quantities towards the end of the operation, shaking well after each addition until a soft lather is obtained, which if the bottle is placed at rest on its side, remains continuous over the whole surface for five minutes.

The soap should not be added in large quantities at a time, even if the volume required is approximately known.

If magnesium salts are present, a kind of scum (simulating a lather) will be seen before the reaction is completed. The character of this scum must be carefully watched, and the soap solution added very carefully, with an increased amount of shaking after each addition. The point when the false lather due to the magnesium salt ceases and the true persistent lather is produced is comparatively easy to distinguish.

If more than 23 cc. of the soap solution are consumed by the 100 cc. of water, a smaller quantity of water should be taken (say 50 or 25 cc.) and made up to 100 cc. with distilled water, recently boiled. In such case the quantity of soap solution used must be multiplied by 2 or 4.

If the first-mentioned soap solution is used each cc. represents 0.00125 gm. If the second solution is used each cc. represents 0.001 gm. of  $\text{CaCO}_3$ , and if 100 cc. of water are acted upon each cc. represents 1 part of  $\text{CaCO}_3$  in 100,000.

If 70 cc. of water are acted upon, instead of 100 cc., each cc. of soap solution used represents 1 gm. per 70,000 cc., which corresponds to 1 gr. per imperial gallon (70,000 grs.) or 1 degree of hardness.

These estimations are, however, only approximate, for the lather does not form until the reaction between the soap and the calcium in the water is completed, and then the quantity of soap solution required to produce the lather depends upon its strength.

Dr. Clark, the originator of this method, has shown that 1000 grains of distilled water (free from hardness)



require 1.4 measures of soap solution, each measure being the volume of 10 grains of distilled water at 16° C.

*For Permanent Hardness.*—To determine the hardness after boiling, a measured quantity of water must be boiled briskly for half an hour, adding distilled water from time to time to make up the loss by evaporation. At the end of the half-hour allow the water to cool, make up to its original volume with recently boiled and cooled distilled water, filter rapidly, and test in the same manner as described above. One half or one cc. is deducted from the soap solution used, for the calculation.

Among German chemists it is customary to designate the soap-destroying power equivalent to 1 part of CaO in 100,000, as one degree of hardness.

Among French chemists each degree of hardness represents 1 part of CaCO<sub>3</sub> in 100,000.

#### INTERPRETATION OF RESULTS.

**Statement of Analysis.**—The composition of water is generally expressed in terms of a unit of weight in a definite volume of liquid, but no fixed standard is used, the proportions being expressed by some analysts in parts per million, by others in parts per hundred thousand. Sometimes, generally by English chemists, the figures are given in grains per imperial gallon of 70,000 grains; less frequently, in grains per U. S. gallon of 58,328 grains.

In order to pass judgment upon the analytical results from a sample of water, the analyst must know to which class of water it belongs—whether river-water, well-water, or artesian-well water. He must know something of the soil and geological character of the locality from which the water is obtained, as well as



other conditions of the locality which might affect the quality of the water, such as proximity of stables, cess-pools, sewers, factories, etc.

**Color.**—Water of the highest purity is clear, colorless, odorless, and nearly tasteless. But the color of water is no indication of its quality. A turbid or colored water is not necessarily a dangerous one, neither is a clear, colorless water always a safe water.

**Odor.**—For comfort, if for nothing else, potable water should be free from odor. Water sometimes has an unpleasant odor and taste, yet it may be used with perfect safety for domestic purposes. At other times the odor may give rise to suspicions which a subsequent examination may confirm. Thus by the odor alone the safety of the water cannot be told.

**Total Solids.**—This is intended to represent the total solid matters dissolved in the water; but since much of the organic matter as well as some of the inorganic matter is volatilized by evaporation, the total solids obtained by this method are only the total non-volatile solids. The indication is thus lower than it should be. On the other hand, certain salts, especially calcium sulphate, retain water of crystallization, thus producing an effect in the opposite direction.

The total solids so obtained, contain both organic and inorganic matters, either of which may be injurious or not. Mineral waters contain large quantities of inorganic salts. Much smaller quantities of total solids in other waters might indicate pollution.

Large quantities of mineral solids, especially of marked physiological action, are known to render water non-potable; but no *absolute* maximum or minimum can be assigned as the limit of safety. An arbitrary

limit has, however, been fixed by sanitary authorities of 60 parts per 100,000 ; and if the solid residue does not exceed 57 parts per 100,000, there is no reason for rejecting a water. Many waters, especially artesian waters, which are in constant use, contain much larger quantities.

The loss on ignition should never reach 50 per cent of the total residue.

**Chlorine** in potable waters is very largely derived from sodium and potassium chlorides of urine and sewage.

Food contains considerable amounts of chlorides, and still more is added by way of condiment in the shape of salt. The chlorine thus taken into the system is again thrown off in the excreta, and thus appears in the sewage ; hence the presence of large quantities of chlorine in water is taken as an indication of pollution. Urine contains about 500 parts of chlorine per 100,000. The average quantity found in sewage is about 11.5 parts per 100,000. Over 5 parts per 100,000 of chlorine in a water may be considered, in most cases, to be due to pollution of the water by sewage or animal excretions. The chlorine itself is not a dangerous constituent of water, but its presence in large quantities is an unfavorable indication. Nevertheless too much dependence must not be put upon the amount of chlorine in water as a means of judging of its purity, for dangerous vegetable matter may exist in it without its presence being indicated by chlorine. The maximum amount of chlorine per 100,000, given by the Rivers Pollution Commission, is 21.5 parts, the minimum 6.5 parts. Various conditions, however, which affect the proportion of chlorine, such as the

nature of the strata through which the water passes, proximity to the sea, etc., must be taken into account.

**Nitrogen in Ammonia.**—Ammonium compounds are usually the result of the spontaneous putrefactive fermentation of nitrogenous organic matter; nitrites are then formed, and finally nitrates. Ammonium compounds may also result from the reduction of nitrites and nitrates in the presence of excess of organic matter. Therefore in either case the presence of ammonia suggests contamination.

This fact is so generally conceded that the estimation of ammonia in water, is a very important part of the sanitary examination.

In the water from deep wells an excess of ammonia is nearly always found, but its presence here cannot always be considered an adverse condition, since it is derived largely from the decomposition of nitrates, and shows previous contamination; but the water having undergone extensive filtration and oxidation, its organic matter is presumably converted into harmless bodies.

Rain-water often contains large proportions of ammonium compounds, which it dissolves out of the air in its descent; but here also, this fact cannot condemn the water, since it does not indicate contamination with dangerous organic matter.

An average of 71 samples of rain-water collected in England contained 0.05 parts per 100,000, including an exceptional maximum of 0.21 parts.

Fischer ("Chemische Technologie des Wassers") gives two analyses of typically good wells, containing respectively 0.048 and 0.044 parts per 100,000, and of

two typically bad shallow wells, containing respectively 0.084 and 2.227 parts per 100,000.

**Albuminoid Ammonia.**—If water yields no albuminoid ammonia it is free from recently added organic contamination. If it contain more than 0.01 part per 100,000 it is looked upon as suspicious, and when it reaches 0.015 parts per 100,000 it is to be condemned. When free ammonia is present in considerable quantity, then the albuminoid ammonia becomes suspicious when it reaches 0.005 parts per 100,000. An opinion should not, however, be formulated without a knowledge of the source of the water; for, as has been said before, free ammonia may exist in large quantities in deep wells without indicating contamination. Wanklyn gives the following standards:

High purity.. . . .	.000	to	.0041	of albuminoid ammonia per 100,000
Satisfactory purity	.0041	to	.0082	“ “ “ “ “
Impure . . . . .	over	.0082	“ “ “ “ “	

In the absence of free ammonia he does not condemn a water unless the albuminoid ammonia exceeds .0082 parts per 100,000; but he condemns a water yielding 0.0123 parts of albuminoid ammonia, under all circumstances.

**Nitrogen as Nitrates.**—Nitrates are normally present in all natural waters, and are derived chiefly from the oxidation of *animal* matters. The nitrogen of organic matters liberated by putrefaction, is first converted into ammonia; then this is oxidized into nitrous, and finally into nitric acid. These changes are due partially to direct oxidation and partially to certain micro-organisms which have the power of converting nitrogenous organic matter into nitrites and nitrates.

Nitrates and nitrites in themselves, in the quantity in which they exist in water, are perfectly harmless. They are, however, an indication of previous contamination; and many analysts believe that a water which has once been contaminated is always open to suspicion. Others consider them of little importance in determining the impurity of a water. Water which is laden with organic matter is purified by percolating through the ground, the nitrogenous matter being converted into nitrates; therefore deep wells may contain large quantities of nitrates without being essentially impure, while the water from shallow wells should be condemned if the nitrates are excessive.

Certain strata, as the chalk formation, yield large amounts of nitrates to water. If the nitrogen as nitrates exceeds 0.6 parts per 100,000 the water is suspected.

**Nitrogen as Nitrites.**—Some chemists regard the presence of nitrites as an indication that the oxidation of the dangerous compounds has probably been incomplete, and accordingly condemn water in which nitrites are found. Leeds places the nitrites in American rivers at .03 per 100,000. The average in good waters is placed at about .0014 per 100,000. When the quantity exceeds .02 parts per 100,000 it is considered an indication of previous contamination.

**Oxygen Consuming Power.**—This is intended to represent the oxidizable organic matter in the water. But there are other substances in water besides organic matters which absorb oxygen, namely, nitrites, which are thus oxidized to nitrates; ferrous salts, which are oxidized into ferric salts; etc. Thus the oxygen-consuming power does not represent the organic matter

alone. However, a water having a high oxygen-consuming power may be considered as polluted.

The following basis for interpreting results of this method are given by Frankland and Tidy:

	Oxygen absorbed in 3 hours.		
High organic purity.....	.05	parts	per 100,000
Medium purity.....	.05 to .15	"	"
Doubtful.....	.15 to .21	"	"
Impure.....	over .21	"	"

**Phosphates.**—Sewage contains large amounts of phosphates, but water usually contains alkaline or earthy carbonates, which precipitate the phosphates; therefore the absence of phosphates does not indicate purity. But their presence *may* indicate sewage contamination. .06 parts per 100,000 is regarded with suspicion (calculated as  $\text{PO}_4$ ).

**Hardness.**—On account of the presence of considerable amounts of calcium compounds in our food sewage is usually very hard, containing especially calcium sulphate. The hardness of water, therefore, has some bearing upon the question as to whether the water is probably polluted with sewage or not. But water may be hard, yet otherwise perfectly pure. The test for the degree of hardness is therefore of little importance in determining sewage, as the figures below show that water uncontaminated by sewage may be very hard.

	Temporary.	Permanent.
Rain-water, average.....	0.3	1.7
Highest from different geological formations ...	38.6	48.5
From 272 samples of water from shallow and polluted wells :		
Minimum.....	0	3.8
Maximum.....	52	164.3
Average.....	19	31.5



The above figures are parts in 100,000. The hardness has, however, much significance from an economic point of view. Hard water is objectionable for domestic purposes in washing, because of its soap-destroying power, and for manufacturing purposes in boilers. It has no bad effect upon the health, but is by some considered wholesome.

**Standards.**—Certain standards have been fixed by some chemists for determining the purity or impurity of water, according to which if certain figures are exceeded the water is to be condemned.

*Dr. Tidy's* classification depends upon the amount of oxygen consumed, from potassium permanganate, after standing three hours.

- |                            |      |           |
|----------------------------|------|-----------|
| 1. Great organic purity... | 0    | to 0.05   |
| 2. Medium purity.....      | 0.05 | " 0.15    |
| 3. Doubtful.....           | 0.15 | " 0.21    |
| 4. Impure.....             |      | over 0.21 |

These standards are applied to waters other than upland surface-waters, in which larger quantities of oxygen may be absorbed.

*Wanklyn's* standard is based upon the indications of the amounts of free and albuminoid ammonia, as follows:

- |                              |       |            |                                 |
|------------------------------|-------|------------|---------------------------------|
| 1. Extraordinary purity..... | 0     | to 0.005   | part albuminoid $\text{NH}_3$ . |
| 2. Satisfactory purity.....  | 0.005 | to 0.010   | " " "                           |
| 3. Dirty.....                |       | over 0.010 | " " "                           |

If the albuminoid ammonia exceeds 0.005 parts per 100,000 the free ammonia must be taken into account. If the free ammonia is in large quantity it is a suspicious sign. If it is in small quantity or altogether absent, the water should not be condemned, unless the



albuminoid ammonia is something like 0.010 parts per 100,000; while over 0.015 should condemn the water absolutely.

The following is a list of analyses of waters which were pronounced good. The results are given in parts per 100,000.

	I.	II.	III.	IV.
Chlorine.....	0.877	1.333	9.294	1.578
Free ammonia.....	0.0004	none	0.002	0.0002
Albuminoid ammonia.....	none	0.0006	0.005	0.0022
Oxygen absorbed (in 3 hours)	0.0054	0.0016	0.0255	0.0008
N in nitrates and nitrites....	0.2525	0.3376	0.0107	0.2633
Total hardness.....	19.23	14.0000	13.33	2.079
Permanent hardness.....	3.715	3.934	3.060	1.980
Organic and volatile matters	1.5	1.7	trace	2.100
Total solids (dried at 230° F.)	24.4	27	37.40	9.40

The following were pronounced bad :

	I.	II.	III.	IV.
Chlorine.....	0.316	62.43	4.208	28.230
Free ammonia.....	0.0196	0.278	none	0.0105
Albuminoid ammonia.....	0.0678	0.0030	0.0105	0.0395
Oxygen absorbed (in 3 hours)	0.2912	0.133	0.0165	0.2110
N in nitrates and nitrites....	0.0283	none	0.247	0.6210
Total hardness.....	6.940	27.72	13.068	50.00
Permanent hardness.....	3.5	23.76	2.574	32.670
Organic and volatile matters	0.5	19.5	trace	8.00
Total solids (dried at 230° F.)	15.60	156.20	30.50	146.50

I, Back of slaughter-house ; II, Drive-well on beach ; III, Well ; IV, Well 30 feet deep.

## CHAPTER XV.

## ESTIMATION OF CARBONIC-ACID GAS IN THE ATMOSPHERE.

THIS is done by Pettenkofer's method. A glass globe or bottle holding from 5 to 10 litres is filled with the air to be tested, by means of a bellows; baryta water of known strength is then introduced in convenient quantity.

The bottle is then securely closed and set aside for about one hour, rotating it at intervals, so that the liquid is spread over the entire inner wall of the bottle.

When the time is up the baryta water is emptied out quickly into a beaker, covered carefully with a watch-glass, and when the barium carbonate has subsided a portion of the clear liquid is withdrawn and titrated with  $\frac{N}{10}$  oxalic-acid solution. The difference between

the quantity of oxalic-acid solution required to neutralize the barium-hydroxide solution, before and after contact with the air, is the quantity equivalent to the carbonic-acid gas absorbed.

*The Baryta-water* is made by dissolving about 7 gms. of pure crystallized barium hydroxide in 1000 cc. of distilled water.

This solution, being prone to absorb  $\text{CO}_2$  out of the air, must be kept in a special bottle, such as is illustrated in Fig. 23, which prevents access of  $\text{CO}_2$  and

admits of the withdrawal of any quantity of solution without inverting the bottle.

*The Bottle* which is used to collect the air should hold from 5 to 10 litres, and its exact capacity must be known. This may be found by filling the bottle to the bottom of the cork with water and then accurately measuring the water. Before using the bottle it must be absolutely dry.

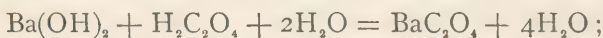
*The Analysis.*—Into the bottle, the capacity of which is exactly known,—we will assume it to be 7100 cc.,—is blown the air to be tested, by means of a bellows.

100 cc. of the baryta-water are then introduced, thus leaving 7000 cc. of air in the bottle.

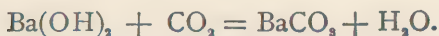
The bottle is now securely closed and set aside for about half an hour, rotating it occasionally so as to spread the liquid over the entire inner wall of the bottle. While waiting for the half-hour to expire, a convenient quantity of baryta-water is taken and its strength compared to decinormal oxalic-acid solution by titrating with the latter, using phenolphthalein as indicator.

50 cc. of baryta-water is a convenient quantity. This is placed in a beaker, a few drops of phenolphthalein added, and then titrated with the  $\frac{N}{10}$  acid solution until the color just disappears.

Let us assume that 40 cc. of the latter were consumed; 80 cc. will then be consumed by 100 cc. of baryta-water.



$$\begin{array}{r} 2)170.9 \\ 10) 85.45 \\ \hline 8.545 \text{ gms.} \end{array} \qquad \begin{array}{r} 2)126 \\ 10) 63 \\ \hline 6.3 \text{ gms. or } 1000 \text{ cc.} \end{array} \quad \frac{N}{10} \text{ V. S.}$$



$$\begin{array}{r} 2)170.9 \\ 10)85.45 \\ \hline 8.545 \text{ gms.} \end{array} \quad \begin{array}{r} 2)44 \\ 10)22 \\ \hline 2.2 \text{ gms.} \end{array}$$

These equations show that 2.2 gms. of carbon dioxide will neutralize as much barium hydroxide as 1000 cc. of  $\frac{N}{10}$  oxalic-acid solution. And thus each cc.

of the  $\frac{N}{10}$  oxalic-acid solution is chemically equivalent to 0.0022 gm. of carbon dioxide; therefore 100 cc. of the baryta-water is capable of absorbing  $80 \times .0022$  gm. = 0.176 gm. of  $\text{CO}_2$ .

The next step is to determine the quantity of  $\text{CO}_2$  that was absorbed by the 100 cc. of baryta-water, which was introduced into the bottle of air.

The liquid is poured out of the bottle into a small beaker, carefully covered with a watch-glass, and the barium carbonate allowed to settle. Then 50 cc. of the clear supernatant liquid are drawn out of the beaker by means of a pipette, treated with a few drops of phenolphthalein T. S., and titrated with the  $\frac{N}{10}$  oxalic acid V. S. until the red color is just discharged. Note the number of cc. consumed, double it, and deduct this number from 80, the quantity which 100 cc. of baryta-water consumed before being brought in contact with  $\text{CO}_2$ .

*Example.*—Assuming that 30 cc. of the oxalic-acid solution were required by the 50 cc. of the baryta-water after exposure, the 100 cc. then would require 60. There is thus a loss of alkalinity equivalent to 20

cc. of  $\frac{N}{10}$  oxalic acid V. S. This is due to the absorption of carbon dioxide, which neutralizes the hydroxide by forming a carbonate.

Now since each cc. of  $\frac{N}{10}$  oxalic acid V. S. is chemically equivalent to 0.0022 gm. of  $\text{CO}_2$ , the baryta-water must have absorbed

$$20 \times 0.0022 \text{ gm.} = 0.044 \text{ gm. of } \text{CO}_2.$$

Therefore the 7000 cc. of air which the bottle held contained 0.044 gm. of  $\text{CO}_2$ .

In stating the result of an analysis the quantity of  $\text{CO}_2$  by volume in 10,000 cc. of air is generally given.

In the above case 7000 cc. of air contained 0.044 gm. of  $\text{CO}_2$ ; 10,000 cc. of this same air, then, contains

$$\frac{0.044 \times 10,000}{7000} \quad \text{or} \quad \frac{0.044 \times 10}{7} = 0.0628 \text{ gm.}$$

If several bottles are in use it is convenient to mark upon them the multiplier and divisor; thus:

$$\frac{10,000}{7000} \quad \text{or} \quad \frac{10}{7}.$$

In calculating the volume of a gas, the temperature and pressure must be taken into account.

By referring to the following table the volume occupied by 0.001 gm. of  $\text{CO}_2$  at different temperatures can be seen.

The volume of 0.0628 gm. of  $\text{CO}_2$  at 16° C. is

$$\frac{0.0628 \times 0.53843}{0.001} = 33.81 \text{ cc.}$$

TABLE SHOWING VOLUME OF .001 GM. OF CARBON DIOXIDE AT VARIOUS TEMPERATURES.

C.°	F.°	Cc.	C.°	F.°	Cc.
0	32	0.50863	13	55.4	0.53314
1	33.8	0.51049	14	57.2	0.53471
2	35.6	0.51235	15	59	0.53657
3	37.4	0.51451	16	60.8	0.53843
4	39.2	0.51608	17	62.6	0.54030
5	41	0.51794	18	64.4	0.54216
6	42.8	0.51980	19	66.2	0.54402
7	44.6	0.52167	20	68	0.54589
8	46.4	0.52353	21	69.8	0.54775
9	48.2	0.52539	22	71.6	0.54961
10	50	0.52726	23	73.4	0.55177
11	51.8	0.52912	24	75.2	0.55334
12	53.6	0.53098			

If the pressure remains constant, the volume of a gas increases regularly as the temperature increases, and decreases as the temperature decreases. (Charles' Law.)

This expansion or contraction amounts to  $\frac{1}{273}$  of the volume of the gas for each degree centigrade.

Thus by calculation the volume of .001 gm.  $\text{CO}_2$  (0.50863 cc.) at any temperature may be found.

$$\frac{1}{273} \text{ of } .50863 = 0.001863.$$

Then to find the volume at any given C. temperature multiply the degree of temperature by 0.001863, and add the answer to 0.50863.

## CHAPTER XVI.

## ESTIMATION OF ALCOHOL IN TINCTURES AND BEVERAGES.

THE quantity of alcohol contained in *dilute spirit*, which leaves no residue upon evaporation, may be ascertained by taking the sp. gr. and referring to the alcohol table. When taking the specific gravity, the temperature of the liquid should be  $15\frac{5}{8}^{\circ}$  C. ( $60^{\circ}$  F.).

**In Wines, Beer, Tinctures,** and other alcoholic liquids containing vegetable matter, the sp. gr. of the sample is taken at  $15\frac{5}{8}^{\circ}$  C. ( $60^{\circ}$  F.) and noted. A certain quantity (say 100 cc.) is measured off and evaporated to one half, or till all odor of alcohol has passed off, the evaporation being conducted without ebullition, in order that particles of the material may not be carried off by the steam. The liquid left is then diluted with distilled water, cooled to  $60^{\circ}$  F. and made up to the original volume (100 cc.), and the sp. gr. taken. Lastly, we calculate: the sp. gr. before evaporating is divided by the sp. gr. after evaporating, and the quotient will be the sp. gr. of the water and alcohol only of the liquor. Then by referring to the alcohol table the percentage of alcohol contained in the liquor is obtained.

*Example.*—The liquor before evaporating had a sp. gr. of 0.9951; after evaporation and dilution to 100 cc. the sp. gr. was found to be 1.0081.



$$\frac{.9951}{1.0081} = 0.987, \text{ the sp. gr. of the contained spirit.}$$

Then by referring to the table we will find that this sp. gr. corresponds to 7.33 per cent., by weight, of absolute alcohol.

*Another Way* is to boil the liquid in a retort, condense the vapor, and when all the alcohol has passed over add sufficient water to the distillate to make up the original volume, at the temperature of  $15\frac{5}{9}^{\circ}$  C. ( $60^{\circ}$  F.). Then, by taking the sp. gr. of this diluted distillate, the quantity of absolute alcohol is found by reference to the table. This latter method requires the taking of the sp. gr. but once and gives more accurate results.

TABLE FOR ASCERTAINING THE PERCENTAGES RESPECTIVELY OF ALCOHOL BY WEIGHT, BY VOLUME, AND AS PROOF SPIRIT, FROM THE SPECIFIC GRAVITY.

*Condensed from the excellent Alcohol Tables of Mr. Gehner in the "Analyst," vol. v. pp. 43-63.*

Specific Gravity 15.5°.	Absolute Alcohol by w'ght. Per cent.	Absolute Alcohol by vol'me Per cent	Proof Spirit. Per cent.	Specific Gravity 15.5°.	Absolute Alcohol by w'ght. Per cent.	Absolute Alcohol by vol'me Per cent.	Proof Spirit. Per cent.
1.0000	0.00	0.00	0.00	.9489	35.95	41.90	73.43
.9999	0.05	0.07	0.12	.9479	35.55	42.45	74.39
.9989	0.58	0.73	1.28	.9469	36.06	43.01	75.37
.9979	1.12	1.42	2.48	.9459	36.61	43.63	76.45
.9969	1.75	2.20	3.85	.9449	37.17	44.24	77.53
.9959	2.33	2.93	5.13	.9439	37.72	44.86	78.61
.9949	2.89	3.62	6.34	.9429	38.28	45.47	79.68
.9939	3.47	4.34	7.61	.9419	38.83	46.08	80.75
.9929	4.06	5.08	8.90	.9409	39.35	46.64	81.74
.9919	4.69	5.86	10.26	.9399	39.85	47.18	82.69
.9909	5.31	6.63	11.62	.9389	40.35	47.72	83.64
.9899	5.94	7.40	12.97	.9379	40.85	48.26	84.58
.9889	6.64	8.27	14.50	.9369	41.35	48.80	85.53
.9879	7.33	9.13	15.99	.9359	41.85	49.34	86.47
.9869	8.00	9.95	17.43	.9349	42.33	49.86	87.37
.9859	8.71	10.82	18.90	.9339	42.81	50.37	88.26
.9849	9.43	11.70	20.50	.9329	43.29	50.87	89.15
.9839	10.15	12.58	22.06	.9319	43.76	51.38	90.03
.9829	10.92	13.52	23.70	.9309	44.23	51.87	90.89
.9819	11.69	14.46	25.34	.9299	44.68	52.34	91.73
.9809	12.46	15.40	26.99	.9289	45.14	52.82	92.56
.9799	13.23	16.33	28.62	.9279	45.59	53.29	93.39
.9789	14.00	17.26	30.26	.9269	46.05	53.77	94.22
.9779	14.91	18.36	32.19	.9259	46.50	54.24	95.05
.9769	15.75	19.39	33.96	.9249	46.96	54.71	95.88
.9759	16.54	20.33	35.63	.9239	47.41	55.18	96.70
.9749	17.33	21.29	37.30	.9229	47.86	55.65	97.52
.9739	18.15	22.27	39.03	.9219	48.32	56.11	98.34
.9729	18.92	23.19	40.64	.9209	48.77	56.58	99.10
.9719	19.75	24.18	42.38	.9199	49.20	57.02	99.93
.9709	20.58	25.17	44.12				
.9699	21.38	26.13	45.79	.9198	49.24	57.06	100.00Ps
.9689	22.15	27.04	47.39				
.9679	22.92	27.95	48.98	.9189	49.68	57.49	100.76
.9669	23.69	28.86	50.57	.9179	50.13	57.97	101.59
.9659	24.46	29.76	52.16	.9169	50.57	58.41	102.35
.9649	25.21	30.65	53.71	.9159	51.00	58.85	103.12
.9639	25.93	31.48	55.18	.9149	51.42	59.26	103.85
.9629	26.60	32.27	56.55	.9139	51.83	59.68	104.58
.9619	27.29	33.06	57.94	.9129	52.27	60.12	105.35
.9609	28.00	33.89	59.40	.9119	52.73	60.56	106.15
.9599	28.62	34.61	60.66	.9109	53.17	61.02	106.93
.9589	29.27	35.35	61.95	.9099	53.61	61.45	107.69
.9579	29.93	36.12	63.30	.9089	54.05	61.88	108.45
.9569	30.50	36.76	64.43	.9079	54.52	62.36	109.28
.9559	31.06	37.41	65.55	.9069	55.00	62.84	110.12
.9549	31.69	38.11	66.80	.9059	55.45	63.28	110.92
.9539	32.31	38.82	68.04	.9049	55.91	63.73	111.71
.9529	32.94	39.54	69.29	.9039	56.36	64.18	112.49
.9519	33.53	40.20	70.46	.9029	56.82	64.63	113.26
.9509	34.10	40.84	71.58	.9019	57.25	65.05	113.99
.9499	34.57	41.37	72.50				

Specific Gravity 15.5°.	Absolute Alcohol by w'ght. Per cent.	Absolute Alcohol by vol'me Per cent.	Proof Spirit. Per cent.	Specific Gravity 15.5°.	Absolute Alcohol by w'ght. Per cent.	Absolute Alcohol by vol'me Per cent.	Proof Spirit. Per cent.
.9009	57.67	65.45	114.69	.8429	82.19	87.27	152.95
.8999	58.09	65.85	115.41	.8419	82.58	87.58	153.48
.8989	58.55	66.29	116.18	.8409	82.96	87.88	154.01
.8979	59.00	66.74	116.06	.8399	83.35	88.19	154.54
.8969	59.43	67.15	117.68	.8389	83.73	88.49	155.07
.8959	59.87	67.57	118.41	.8379	84.12	88.79	155.61
.8949	60.29	67.97	119.12	.8369	84.52	89.11	156.16
.8939	60.71	68.36	119.80	.8359	84.92	89.42	156.71
.8929	61.13	68.76	120.49	.8349	85.31	89.72	157.24
.8919	61.54	69.15	121.18	.8339	85.69	90.02	157.76
.8909	61.96	69.54	121.86	.8329	86.08	90.32	158.28
.8899	62.41	69.96	122.61	.8319	86.46	90.61	158.79
.8889	62.86	70.40	123.36	.8309	86.85	90.90	159.31
.8879	63.30	70.81	124.00	.8299	87.23	91.20	159.82
.8869	63.74	71.22	124.80	.8289	87.62	91.49	160.33
.8859	64.17	71.62	125.51	.8279	88.00	91.78	160.84
.8849	64.61	72.02	126.22	.8269	88.40	92.08	161.37
.8839	65.04	72.42	126.92	.8259	88.80	92.39	161.91
.8829	65.46	72.80	127.59	.8249	89.19	92.68	162.43
.8819	65.88	73.19	128.25	.8239	89.58	92.97	162.93
.8809	66.30	73.57	128.94	.8229	89.96	93.26	163.43
.8799	66.74	73.97	129.64	.8219	90.32	93.52	163.88
.8789	67.17	74.37	130.33	.8209	90.68	93.77	164.33
.8779	67.58	74.74	130.68	.8199	91.04	94.03	164.78
.8769	68.00	75.12	131.64	.8189	91.39	94.28	165.23
.8759	68.42	75.49	132.30	.8179	91.75	94.53	165.67
.8749	68.83	75.87	132.05	.8169	92.11	94.79	166.12
.8739	69.25	76.24	133.60	.8159	92.48	95.06	166.58
.8729	69.67	76.61	134.25	.8149	92.85	95.32	167.04
.8719	70.08	76.98	134.90	.8139	93.22	95.58	167.50
.8709	70.48	77.32	135.51	.8129	93.59	95.84	167.96
.8699	70.88	77.67	136.13	.8119	93.96	96.11	168.24
.8689	71.29	78.04	136.76	.8109	94.31	96.34	168.84
.8679	71.71	78.40	137.40	.8099	94.66	96.57	169.24
.8669	72.13	78.77	138.05	.8089	95.00	96.80	169.65
.8659	72.57	79.16	138.72	.8079	95.36	97.05	170.07
.8649	73.00	79.54	139.39	.8069	95.71	97.29	170.50
.8639	73.42	79.90	140.02	.8059	96.07	97.53	170.99
.8629	73.83	80.26	140.65	.8049	96.40	97.75	171.30
.8619	74.27	80.64	141.33	.8039	96.73	97.96	171.68
.8609	74.73	81.04	142.03	.8029	97.07	98.18	172.05
.8599	75.18	81.44	142.73	.8019	97.40	98.39	172.43
.8589	75.64	81.84	143.42	.8009	97.73	98.61	172.80
.8579	76.08	82.23	144.10	.7999	98.06	98.82	173.17
.8569	76.50	82.58	144.72	.7989	98.37	99.00	173.50
.8559	76.92	82.93	145.34	.7979	98.69	99.18	173.81
.8549	77.33	83.28	145.96	.7969	99.00	99.37	174.17
.8539	77.75	83.64	146.57	.7959	99.32	99.57	174.52
.8529	78.16	83.98	147.17	.7949	99.65	99.77	174.87
.8519	78.56	84.31	147.75	.7939	99.97	99.98	175.22
.8509	78.96	84.64	148.32				
.8499	79.36	84.97	148.90				
.8489	79.76	85.29	149.44				
.8479	80.17	85.63	150.06				
.8469	80.58	85.97	150.67				
.8459	81.00	86.32	151.27				
.8449	81.40	86.64	151.83				
.8439	81.80	86.96	152.40				
				Absolute Alcohol.			
				.7938	100.00	100.00	175.25

## CHAPTER XVII.

## ESTIMATION OF TANNIN.

G. FLEURY (Jour. Phar. Chim., 1892, 499) proposes to use egg-albumen for estimating tannin in wine and in the petals of red roses.

The hard-boiled egg-albumen is dried at a moderate temperature, and powdered. This is washed with dilute alcohol (10 per cent), very slightly acidulated with tartaric acid, to saturate the alkali. The albumen is again dried, and kept in a well-stoppered bottle.

The method of operation is as follows:

Albumen powder, equal to seven or eight times the quantity of tannin, which is supposed to be present, is added to the liquid in a flat dish. The dish is then set aside for forty-eight hours, stirring occasionally; the liquid must during this time be acid, not alkaline.

The end of the reaction is attained when the liquid ceases to give a color with ferric chloride T. S.

The powder is then collected on a filter, washed with very dilute alcohol, and then dried at  $100^{\circ}$  C. At the same time a sample of the original powder is dried and weighed, to determine the amount of water it contains.

The increase in weight of the albumen which was in contact with the tannin, minus the loss of weight of the albumen in the check experiment, gives the weight of tannin present.

This method is not available for determining the

tannid in nutgalls, because the absorption by the albumen is incomplete and too slow. In testing, it must be borne in mind that gallic acid is not absorbed by the albumen, and consequently still gives its reaction with ferric chloride.

#### ESTIMATION OF TANNIN IN BARKS, ETC. (LÖWENTHAL'S METHOD.)

The principle of this method depends upon the oxidation of the tannic acid, together with other easily oxidizable substances, by titrating with potassium permanganate.

The total amount of such substances is thus found, and expressed by a known volume of permanganate. The actual available tannin is then removed by gelatine or glue, and another titration made, to determine the amount of oxidizable matters other than tannin.

The difference between the amounts of permanganate solution used in the two titrations gives the amount of tannin present which is available for tanning purposes, expressed in terms of permanganate.

**Solutions Required.**—1.  $\frac{N}{30}$  *Potassium Permanganate V.S.* (1.05 gm. per litre).

2. *Indigo Solution.*—6 gms. of pure precipitated indigo and 50 cc. of concentrated sulphuric acid are dissolved in sufficient water to make one litre.

3. *Glue and Salt Solution.*—25 gms. of good transparent glue are macerated in cold water, and then heated to dissolve; the solution is then made up to one litre, and saturated with common salt. The solution should be filtered clear when used.

4. *Acidified Solution of Common Salt*.—This is a saturated solution of common salt, containing in one litre 25 cc. of sulphuric acid.

**The Analysis.**—20 gms. of the bark or 10 gms. of sumach are boiled with several portions of water until exhausted, and the solution when cold is made up to one litre.

10 cc. of this solution are diluted to 1000 cc.; 25 cc. of the indigo solution are added, and the permanganate solution then run in, drop by drop, from a burette, stirring constantly, until the blue color changes to yellow, and the number of cc. of permanganate solution consumed noted.

25 cc. of the indigo solution are now taken and diluted to 1000 cc., titrated with permanganate, and the number of cc. again noted. By deducting this number from the number of cc. used in the first titration, the quantity of permanganate required by the tannin and the other oxidizable substances in the 10cc. of solution taken is found.

The next step is to deprive a portion of the tannin solution of its tannin, and again titrate.

100 cc. of the tannin solution are treated with 50 cc. of the glue and salt solution, and, after stirring, 100 cc. of the acidulated salt solution are added, the mixture stirred again, and set aside for several hours. The glue absorbs the tannin out of solution. The solution is then filtered. The filtrate should be perfectly clear.

Of this filtrate take 50 cc. (containing 20 cc. of the tannin solution), mix with 25 cc. of the indigo solution, and titrate with the permanganate solution as before, noting the number of cc. consumed.

Another 25 cc. of the indigo solution are now taken,



diluted as in the other trial, and again titrated with permanganate. By deducting the number of cc. so obtained from the number required by the 50 cc. of filtrate, the quantity required by the oxidizable matter other than tannic acid in the 20 cc. of tannin solution is obtained. Therefore one half of this quantity, when deducted from the quantity of permanganate solution representing the total oxidizable matter in 10 cc. of the tannin solution, gives the quantity of permanganate which was effected by the tannin above.

Duplicate titrations should always be made, and should agree within 0.1 or 0.2 cc. of the permanganate solution.

Thus far we have only the tannin value (expressed in terms of permanganate), of 10 cc. of the original solution, representing  $\frac{1}{100}$  of the material under examination.

The permanganate solution may be compared with a standard solution of the purest gallo-tannic acid obtainable, or with any tannin of known value, and thus a coefficient obtained.

According to the experiments of Neubauer, 63 gms. of pure crystallized oxalic acid (equivalent to 31.4 gms. potassium permanganate) correspond to 41.57 gms. of purified gallo-tannic acid (nutgall tannin). And Oser found that 63 gms. of oxalic acid correspond to 62.355 gms. of querci-tannic acid (oak-bark tannin). These coefficients are now largely used.

Based upon these figures each cc. of  $\frac{N}{30}$  permanganate solution represents .0013856 gm. of gallo-tannin, or .0020785 gm. of querci tannin. In most analyses, however, especially when the composition of the tannin is not exactly known, it is expressed as oxalic acid.

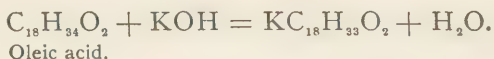


## CHAPTER XVIII.

## ESTIMATION OF OLEIC ACID.

OLEIC acid may be estimated volumetrically by standard solution of potassa or soda, using phenolphthalein as an indicator.

The reaction is expressed by the following equation:



$$282 \text{ gms.} \quad 56 \text{ gms. or } 1000 \text{ cc. } \frac{\text{N}}{1} \text{ KOH.}$$

Thus each cc. of the normal alkali solution consumed represents 0.282 gm. of oleic acid.

**Estimation of Oleic Acid.**—One gramme of the impure fatty acid is saponified in a basin by heating with a slight excess of alcoholic potash, till dissolved, and then diluted with water. This solution is treated with acetic acid drop by drop, until on stirring a faint *permanent* turbidity ensues. Dilute solution of potassium hydrate is then stirred in drop by drop till the liquid just clears up, and then solution of plumbic acetate is stirred in until precipitation ceases. The precipitate having been allowed to settle, the supernatant liquor is poured off and the soap washed once with boiling water. A little clean sand is rubbed up with the soap in the basin, and the whole scraped out and transferred to a "Soxhlet," in which it is thoroughly exhausted with 90

cc. of *pure* ether. The ethereal solution (which now contains only plumbic oleate, the plumbic palmitate and stearate being left insoluble in the Soxhlet) is transferred to a special apparatus, sold by apparatus vendors as "Muter's oleine tube." This is a graduated and stoppered tube holding 120 cc., and having a spout and stop-cock at 30 cc. from its base. Previously to introducing the ether, place 20 cc. of dilute hydrochloric acid (1 in 3) into the tube, and then make up the whole with ether-rinsings of the basin to the 120-cc. mark. Close the tube, shake well, and set aside. When settled, note the full volume of the ethereal solution of oleic acid, and run off an aliquot part from the tap into a weighed dish, evaporate, dry in the water-oven, and weigh. Finally calculate this weight to that of the whole bulk of ethereal solution previously noted, thus getting the amount of real oleic acid present in the gramme of crude acid started with. [From Muter's "Analytical Chemistry."]

## CHAPTER XIX.

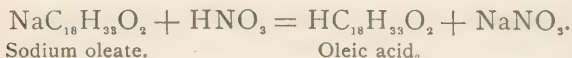
## ANALYSIS OF SOAP.

**Estimation of Water and Volatile Matters.—**

(a) 10 gms. of the soap are dried to a constant weight at  $100^{\circ}$  C. and carefully weighed; the loss of weight = water.

(b) *Free Fats*.—The dried soap obtained as above, is exhausted with petroleum ether of low boiling-point. The petroleum ether is then evaporated off and the residue weighed: this is the weight of the fat contained in 10 gm. of the soap.

(c) *Fatty Acids*.—The residue from (b) which is free from fat and which represents 10 gms. of the soap, is weighed and half of it dissolved in water. Normal nitric acid is then added in excess to liberate the fatty acids. These are collected on a tared filter, dried and weighed. This weight when doubled gives the amount of fatty acids in 10 gms. of the soap. The reaction is illustrated by this equation:



The acid filtrate is now titrated with normal soda or potash, using phenolphthalein as an indicator. The difference between the volumes of acid and alkali solutions used gives roughly the quantity of total alkali.

(d) *Chlorides and Sulphates*.—The residual neutral

liquid from the above, is divided into two equal parts, in one of which chlorine is estimated by  $\frac{N}{10} \text{AgNO}_3$ , using potassium chromate.

In the other sulphuric acid is estimated with barium chloride.

(e) *Free Alkali*, (i.e., the alkali which does not exist as soap).—Ten grammes of the soap are dissolved in hot alcohol, and one drop of phenolphthalein T.S. added; then carbonic-acid gas is passed through the solution until the color disappears. The free alkali is thus converted into sodium carbonate, which is insoluble in alcohol and may be separated by filtration. The residue on the filter is washed with hot alcohol, and then dissolved in a little water and titrated with  $\frac{N}{10}$  acid in the presence of methyl-orange. The number of cc. used multiplied by 0.0031 gives the grammes of free alkali, as  $\text{Na}_2\text{O}$ , in the 10 gms. of soap.

*Combined Alkali*.—The alcoholic solution from the above which contains the combined alkali and the fatty acids, is diluted with a little water, methyl-orange added, and the mixture titrated with decinormal acid. The quantity of combined alkali is thus found. The number of cc. of acid consumed multiplied by 0.0031 gives the quantity as  $\text{Na}_2\text{O}$ .

*Another Way* is to evaporate the alcoholic solution to dryness, the residue then ignited, and the soap thus converted into alkali carbonate. This is dissolved in water and titrated with normal or decinormal acid in the presence of methyl-orange.

The fatty acids are found by using the factor 0.0282 or 0.282. The number of cc. of decinormal acid used

in the above titration when multiplied by 0.0282, or of normal acid when multiplied by 0.282, gives the quantity of fatty acid as oleic. Soaps, however, contain various fatty acids the molecular weights of which differ.

Therefore in estimating the fatty acids volumetrically, the neutralizing power of the acids liberated from soap, expressed in cc. of standard alkali and called the saponification equivalent, is employed.

## CHAPTER XX.

DETERMINATION OF THE MELTING-POINT OF  
FATS.

THE melting-point of a fat can be quickly found by immersing the bulb of a thermometer in the melted fat, then suspending the bulb which is coated with congealed fat in the middle of a beaker of water to which heat is gradually applied, and noting the temperature at which the fatty coat melts from the bulb.

*Another Way.*—Draw out a long capillary tube, Fig. 26. Melt the fat, and draw a small portion of it up into the tube. The melted fat will rise in the tube by capillary attraction. This tube is bound or held against the bulb of a thermometer, and immersed in a beaker of cold water to which heat is applied. The fat is congealed upon immersion in water and becomes opaque. When the temperature of the water is raised to the proper degree, the opaque cylinder of fat melts and becomes transparent. At this point the temperature must be noted. The congealing-point may be found by removing the source of heat and allowing the water to cool gradually, and noting the point at which the fat in the tube again congeals and becomes opaque. The congealing may be hastened by adding cautiously cold water to that in the beaker. The congealing-point will be identical with, or close to the melting-point.



FIG. 26.

## CHAPTER XXI.

## ESTIMATION OF OIL OR FAT IN EMULSIONS AND OINTMENTS.

**Apparatus.**—A test-tube of about eight inches in length, fitted with two good corks, one of which is provided with a wash-bottle arrangement, Fig. 27.

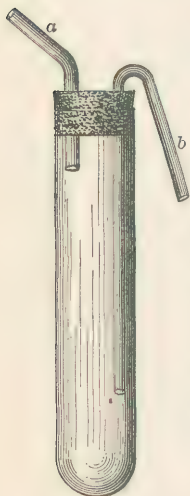


FIG. 27.

**The Process.**—A weighed quantity of the emulsion (2 to 5 gms.) or ointment (1 to 2 gms.) is put into the test-tube, the latter half filled with ether, corked and shaken for about 5 minutes, and set aside so as to allow the liquids to separate. The ethereal solution of the fat or oil, which forms the upper layer, is carefully drawn off into a tared vessel. This is done by inserting the stopper having the wash-bottle arrangement, and gently blowing in the tube *a*. The tube *b* is raised or lowered so that its lower end is slightly above the surface of the lower layer in the tube.

This process is repeated until the fat is completely extracted, which is shown by there being no residue left, when a few drops of the last portion drawn off are evaporated on a watch-glass.



The mixed ethereal solutions are now subjected to evaporation, thus leaving the oil behind. The tared evaporating-dish containing the oil is dried in a water-bath and weighed.

By deducting the weight of the dish when empty from the above weight, the weight of the fat or oil is obtained.

In this way the fat in powdered drugs, in chocolate, in milk, etc., may be estimated. The estimation is more rapid than though not as accurate as, when made by the Soxhlet's extraction apparatus which is illustrated in Fig. 28. Into the tarred flask *A* the ether or other solvent is put. The substance *B*, inclosed in a cartridge of filtering-paper, is introduced into the tube *C*. The latter in turn is connected with an upright condenser *D*. The flask is now heated by a water-bath, and the vapor of the ether rises through *E*, condenses and drops onto the powdered substance in the cartridge. When the instrument has become filled by the solvent to the level of the top of *F*, it runs back into the flask charged with part of the soluble matter. This process repeats itself until the whole of the soluble matter of the substance has been extracted.

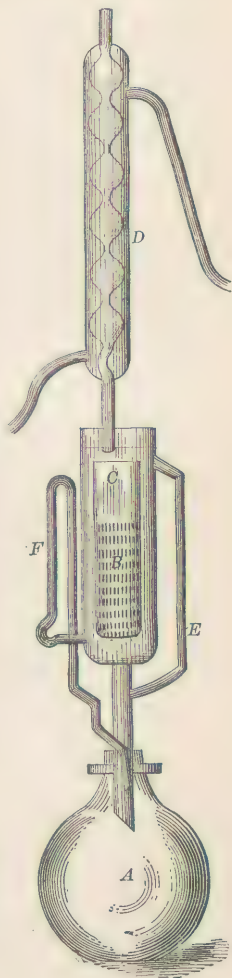


FIG. 28.

The flask is then detached, and the ether evaporated or distilled off; the soluble matter of the original powder being left in the flask. Resinous or sticky substances should be mixed with a little clean sand, in order to facilitate the extraction and prevent clogging up of the apparatus.

## CHAPTER XXII.

## ESTIMATION OF STARCH IN CEREALS, ETC.

THE method about to be described depends upon the fact that when barium hydroxide is brought in contact with starch, an insoluble compound is formed, the formula of which is  $C_{24}H_{40}O_{20}BaO$ . This combination takes place in definite proportions, so that if an excess of barium hydroxide solution is added to the starchy substance, and then the excess estimated, the quantity which combined with and which consequently represents the amount of starch present, is found.

**Solutions Required.**—1. *Decinormal Hydrochloric Acid.* See page 40 (3.637 gm. to 1 liter.) Each cc. represents .00765 gm. of  $BaO$ .

2. *Baryta-water* (barium hydroxide solution), made by dissolving about 7 gms. of pure crystallized barium hydroxide in 1000 cc. of water. Should be kept in a special vessel such as is illustrated in Fig. 23.

**The Process.**—The sample is finely powdered, and 1 gm. weighed out for analysis. This is rubbed up with successive portions of water (using not more than 50 cc.) and transferred to a flask having a capacity of about 150 cc. The flask and contents are now heated upon a water-bath for half an hour to thoroughly gelatinize the starch. If the substance analyzed contains oil, this must first be extracted in a "Soxhlet" apparatus before the water is added,

If free starch is to be experimented with, 0.2 or 0.3 gm. instead of 1 gm. should be taken.

When the starch is gelatinized, the solution is cooled, and 25 cc. of the baryta-water are added. The flask is corked, and well shaken for two minutes; proof spirit is then added to make about 125 cc., the flask again corked, thoroughly shaken, and set aside to settle. While settling a check is made upon 10 cc. of the baryta-water mixed with 50 cc. of recently boiled distilled water, by titrating with decinormal hydrochloric acid, using phenolphthalein as indicator. The number of cc. of  $\frac{N}{10}$  hydrochloric acid V. S. used, is noted, and when multiplied by  $2\frac{1}{2}$  the total strength of the 25 cc. of the baryta-water employed in the analysis is obtained.

When the settling of the insoluble compound is completed, 25 cc. of the clear liquid is drawn off (this is  $\frac{1}{5}$  of the entire quantity) with a pipette and rapidly titrated with the  $\frac{N}{10}$  acid V. S. in the presence of a few drops of phenolphthalein T. S. The number of cc. consumed is noted, multiplied by 5, and then deducted from the number representing the total strength of 25 cc. baryta-water. The difference is the quantity which went into combination with the starch.

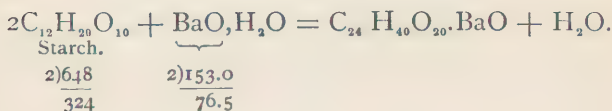
Each cc. of the  $\frac{N}{10}$  hydrochloric acid V. S. represents 0.00765 gm. of  $\text{BaO}_2$ , which is equivalent to 0.0324 gm. of starch.

Therefore by multiplying the number of cc. representing the quantity of baryta which combined with

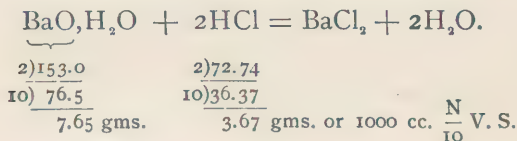
the starch by 0.0324 gm., the quantity of starch present in the sample is obtained.

*Example.*—1 gm. of substance was taken, mixed with 50 cc. of water, 25 cc. of baryta-water, and sufficient proof spirit to make 125 cc. This is set aside and allowed to settle.

The reaction which takes place is as follows :



While settling, the strength of the baryta-water is determined by titrating with decinormal hydrochloric acid V. S., the following equation being applied :



Thus each cc. represents 0.00765 gm. of BaO.

10 cc. of the baryta-water are taken, and 8 cc. of the  $\frac{N}{10}$  acid solution are required to neutralize this. Therefore 25 cc. of baryta-water will require  $2\frac{1}{2} \times 8 \text{ cc.} = 20$  cc. of  $\frac{N}{10}$  acid V. S.

When the settling is completed, 25 cc. of the clear solution is drawn off and titrated with  $\frac{N}{10}$  acid V. S.

We will assume that 2.5 cc. of the  $\frac{N}{10}$  acid V. S. are

required; therefore the entire quantity of solution will neutralize  $5 \times 2.5 \text{ cc.} = 12.5 \text{ cc.}$

The difference between 12.5 cc. and 20 cc. = 7.5 cc., which is the loss of alkalinity expressed in cc. of  $\frac{N}{10}$  acid V. S. Each cc. of alkalinity lost, expressed as  $\frac{N}{10}$  acid V. S., indicates that 0.00765 gm. of BaO went into combination with starch; and since 0.00765 gm. of BaO represents 0.0324 gm. of starch, the substance analyzed contains  $7.5 \times 0.0324 \text{ gm.}$  or 0.243 gm. of starch.

$$\frac{0.243 \times 100}{1} = 24.3\%$$

*Another Method for Estimating Starch* consists in converting it into glucose and then estimating the glucose with Fehling's Solution.

The starch is weighed and boiled in a flask with water containing hydrochloric acid for several hours; the solution is then cooled, neutralized with potassium hydroxide, and diluted so that 1 part of starch, or rather sugar, shall be contained in 200 parts of water. This is put into a burette and titrated into 10 cc. of Fehling's Solution, as described below under Sugar.

## CHAPTER XXIII.

## ESTIMATION OF SUGARS.

**Fehling's Solution.**—(a) *The Copper Solution.*—34.64 gms. of carefully selected small crystals of pure cupric sulphate are dissolved in sufficient water to make, at or near  $15^{\circ}\text{C}$ . ( $59^{\circ}\text{F}$ .), exactly 500 cc. Keep in small well-stoppered bottles.

(b) *The Alkaline-tartrate Solution.*—173 gms. of potassium and sodium tartrate (Rochelle salt) and 125 gms. of potassium hydroxide, U. S. P., are dissolved in sufficient water to make, at or near  $15^{\circ}\text{C}$ . ( $59^{\circ}\text{F}$ .), exactly 500 cc. Keep in small rubber-stoppered bottles.

For use, equal quantities of the two solutions should be mixed at the time required.

10 cc. of the mixed solution is equivalent to

Glucose . . . . .	.050
Maltose . . . . .	.082
Inverted cane-sugar . . . . .	.0475
Inverted starch. . . . .	.045

**The Process.**—0.5 gm. or less of the sugar is dissolved in 100 cc. of water. This liquid is placed in a burette. 10 cc. of the Fehling's Solution are mixed with 50 cc. of water and placed in a porcelain dish over a Bunsen burner and heated to boiling. The sugar solution is then run in from the burette, until all blue color is destroyed.



It is always somewhat difficult to determine the exact point at which the blue color disappears, owing to the presence of the precipitated suboxide of copper. This difficulty may be overcome by the addition of some substance which will prevent the precipitation of the cuprous oxide, such as ammonium hydroxide or potassium ferrocyanide. The disappearance of the blue color can then be readily seen, as the solution remains clear to the end, turning from blue to green, and finally brown, which indicates the end of the reaction.

Professor Bartley reports this method as accurate, reliable, and rapid, provided the solution be not boiled during the reduction. He recommends to add to the Fehling's Solution in the porcelain basin 10 cc. of a 10% freshly prepared solution of potassium ferrocyanide and 30 cc. of water. The ferrocyanide does not precipitate the copper in alkaline solution.

If the sugar to be examined be either glucose, maltose, or lactose, it may be titrated directly; but if it be cane-sugar, it must first be inverted. This is done by dissolving the sugar (0.475 gm.) in about 100 cc. of water, adding 3 or 4 drops of strong hydrochloric acid, and boiling briskly for ten or fifteen minutes. This is then allowed to cool, neutralized with potassium hydroxide, and made up to 100 cc. with water.

*The Calculation.*—10 cc. of Fehling's Solution are always taken; and whatever the quantity of glucose or sugar solution is required to effect reduction, that quantity contains the equivalent of 10 cc. of Fehling's Solution. Thus if 12 cc. of the sugar solution were required to reduce 10 cc. of Fehling's Solution, the 12 cc. contain 0.05 gm. of glucose or 0.082 gm. of maltose,

etc. 100 cc. of the solution therefore contain  $x$  gm. of glucose.

$$\frac{0.5 \times 100}{12} = 0.416 \text{ gm. glucose.}$$

The sugar in urine may be estimated by this process. The urine is placed in the burette and run into the boiling Fehling's Solution in the usual manner. If it contain a large quantity of sugar, it must be diluted two or three times.

In estimating with Fehling's Solution it is well to attach a rubber tube 8 to 12 inches in length to the lower end of the burette, so that the boiling need not be done directly under the burette, and thus cause incorrect readings through the expansion of the liquid therein.

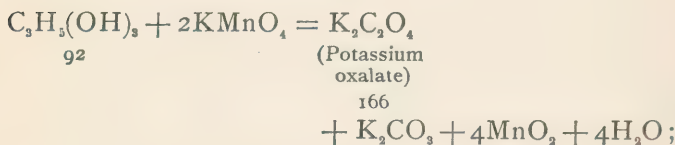
## CHAPTER XXIV.

## ESTIMATION OF GLYCERIN.

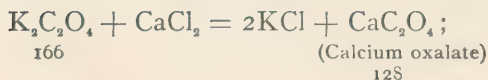
**Glycerin** (Glycerol)  $C_3H_5(OH)_3 = \left\{ \begin{array}{l} 91.79 \\ *92 \end{array} \right.$  —The estimation of glycerin, of fats, etc., may be made by the method of Benedikt and Zsigmondy. This method consists in saponifying the fat and oxidizing the resultant glycerin by permanganate in alkaline solution; thus oxalic acid, carbon dioxide, and water are formed. The excess of permanganate is then destroyed by sulphurous acid or a sulphite, the liquid filtered to separate the manganese dioxide, and the oxalic acid then precipitated by a soluble calcium salt in the presence of acetic acid, and the precipitated calcium oxalate then titrated with permanganate, or after ignition and conversion into carbonate titrated with standard acid solution in the usual way.

Aqueous solutions of glycerin may of course be submitted to the method very easily.

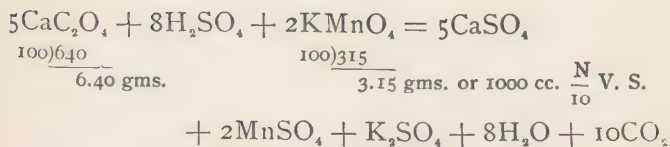
The reactions are as follows:



then



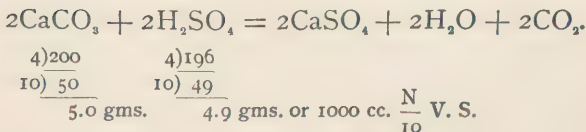
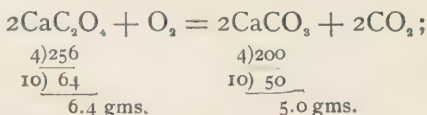
then



Thus 1000 cc.  $\frac{N}{10}$  permanganate solution represents 6.4 gms. of calcium oxalate, which is equivalent to 8.3 gms. of potassium oxalate, which is equivalent to 4.6 gms. of glycerin.

Thus each cc. of the permanganate solution of decinormal strength used up by the calcium oxalate represents .0046 gm. of glycerin.

If the precipitated calcium oxalate is ignited and converted into carbonate, and the carbonate then titrated with decinormal sulphuric or hydrochloric acid, the reactions are as follows:



Thus each cc. of decinormal acid represents 0.005 gm. of  $\text{CaCO}_3$ , or 0.0064 gm. of calcium oxalate, or .0046 gm. of glycerin.

*If experimenting with pure glycerin*, operate upon 10 cc. of a 2% solution. This is diluted with cold water

to about 400 cc., about 10 gms. of caustic potash are added to this, and then a saturated solution of potassium permanganate until the liquid is no longer green, but blue or blackish. An excess does no harm.

The liquid is then boiled for about one hour, and a strong solution of sodium sulphite is added to the boiling liquid until the violet or green color is destroyed; the liquid is then filtered while yet hot, to separate the precipitated manganese dioxide. When cool, it is acidified with acetic acid, and calcium chloride added to precipitate the oxalic acid as calcium oxalate. When the deposition of calcium oxalate is complete it is separated by filtration, and titrated either with permanganate or after ignition with standard sulphuric acid.

The former method is preferable. For this purpose the filter is pierced, and the precipitate rinsed into a porcelain basin; about 10 cc. of dilute sulphuric acid are then added through the funnel slowly, so that it comes into contact with and washes through any of the precipitate that may still cling to it.

The liquid is now diluted to about 200 cc., brought to 60° C., and the decinormal permanganate run in from a burette, slowly, until a faint but distinct pink color appears and remains permanent after stirring; each cc. of the permanganate thus used represents 0.0046 gm. of glycerin.

The process for *estimating the glycerin of fats* is as follows:

Ten grammes of the fat or oil are placed in a strong small bottle together with 4 gms. of pure potassium hydroxide, dissolved in 25 cc. of water; the bottle is then closed with a solid rubber stopper and tied down

firmly with wire; it is then placed in boiling water and heated, with occasional shaking, from six to ten hours, or until the fat or oil is completely saponified. The contents of the bottle are then poured into a beaker and diluted with hot water; this should give a clear solution.

A dilute acid is then added to separate the fatty acids, which are filtered out and the filtrate made up to a given volume.

This solution, which will usually contain 0.2 to 0.5 gm. of glycerin, according to its origin, is transferred to a porcelain basin, diluted with cold water to about 400 cc., and the glycerin estimated as described under the experiment with pure glycerin.

## CHAPTER XXV.

## ESTIMATION OF PHENOL.

**Decinormal Bromine, V. S.** (Koppeschaar's Solution),  $\text{Br} = \left\{ \begin{array}{l} 79.76 \\ *80 \end{array} \right. \cdot \begin{array}{l} 7.976 \\ *8 \end{array} \left\} \text{ gms. in 1 litre.}—$

$\text{KBr} = 118.79$	$\text{NaBr} = 102.76$
$\text{KBrO}_3 = 166.67$	$\text{NaBrO}_3 = 150.64$

This solution does not contain free bromine, but it contains two salts, a bromide and a bromate, which when treated with hydrochloric acid, liberate a definite quantity of bromine.

It is made as follows:

Dissolve 3 gms. of sodium bromate and 50 gms. of sodium bromide (or 3.2 gms. of potassium bromate and 50 gms. of potassium bromide) in sufficient water to make 900 cc.

Transfer 20 cc. of this solution by means of a pipette into a bottle having a capacity of about 250 cc., provided with a glass stopper; add 75 cc. of water, then 5 cc. of pure hydrochloric acid, and immediately insert the stopper.

Shake the bottle a few times, then remove the stopper just sufficiently to quickly introduce 5 cc. of potassium iodide T. S., taking care that no bromine vapor escape, and immediately stopper the bottle.

Agitate the bottle thoroughly, remove the stopper and rinse it and the neck of the bottle with a little water so that the washings flow into the bottle, then



add from a burette decinormal sodium thiosulphate V. S. until the color of the free iodine is nearly all discharged, then add a few drops of starch T. S., and continue the titration with  $\frac{N}{10}$  thiosulphate V. S. until the blue color disappears.

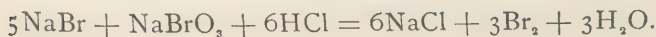
Note the number of cc. of the  $\frac{N}{10}$  sodium thiosulphate V. S. thus used, and dilute the bromine solution so that equal volumes of it and the  $\frac{N}{10}$  sodium thiosulphate V. S. will exactly correspond to each other under the above-mentioned conditions.

*Example.*—Assuming that the 20 cc. of bromine solution required 25.2 cc. of the  $\frac{N}{10}$  thiosulphate to completely absorb the iodine, the bromine solution must be diluted in the proportion of 20 to 25.2; that is, each 20 cc. must be diluted to make 25.2 cc.

Thus if 850 cc. are left, they must be diluted to make 1071 cc., and the solution is decinormal.

A new trial should always be made after diluting, and the bromine solution should correspond, volume for volume, with the decinormal sodium thiosulphate V. S.

The first step in the preparation of this solution is to dissolve the salts; then hydrochloric acid is added, which liberates a definite quantity of bromine, as the equation illustrates:



The stopper should be inserted into the bottle as soon as the hydrochloric acid has been added, in order

that no bromine vapor escape, and the bottle rotated so as to mix the acid thoroughly with the liquid.

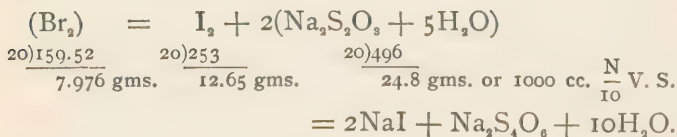
The next step is to determine the quantity of bromine which a definite volume of solution will liberate. The bromine solution should be of such strength that 1000 cc. of it will contain 7.976 gms. of available bromine. Bromine, like chlorine, liberates iodine from potassium iodide, and is estimated in the same manner.

One atomic weight of iodine is liberated by one atomic weight of bromine :



Thus by determining the quantity of iodine liberated the quantity of bromine is found.

The iodine is determined by the  $\frac{\text{N}}{10}$  sodium thiosulphate V. S., one litre of which represents 12.65 gms. of iodine, which is equivalent to 7.976 gms. of bromine, as is shown by the following equation :



**Carbolic Acid**,  $\text{C}_6\text{H}_5(\text{OH}) = \left\{ \begin{array}{l} 93.78 \\ *94 \end{array} \right.$  (Phenol, Phenylhydrate, Hydroxylbenzene, Phenylalcohol).—This is regarded as benzene ( $\text{C}_6\text{H}_6$ ) in which one atom of hydrogen has been replaced by hydroxyl (OH).

*The Valuation of Carbolic Acid according to the U. S. P.* is as follows :

1.563 gm. of the carbolic acid are dissolved in suffi-

cient water to make 1000 cc. 25 cc. of this solution, containing 0.039 gm. of the acid, are transferred to a glass-stoppered bottle having a capacity of about 200 cc.

To this 30 cc. of decinormal bromine V. S., followed by 5 cc. of hydrochloric acid, are added, and the bottle immediately stoppered, and shaken repeatedly during half an hour.

Then the stopper is removed just sufficiently to introduce 5 cc. of a 20-per-cent. aqueous solution of potassium iodide, being careful that no bromine escape.

The bottle is then thoroughly shaken and the neck rinsed with a little water, the washings being allowed to flow into the bottle.

The solution is now ready for titration, and the decinormal sodium thiosulphate is delivered in from a burette, until the iodine is almost completely absorbed; then add a few drops of starch T. S., and continue the titration until the blue color is just discharged.

Note the number of cc. of  $\frac{N}{10}$  thiosulphate V. S. used; deduct this number from 30 cc. (the quantity of  $\frac{N}{10}$  bromine V. S. originally added), and the quantity of  $\frac{N}{10}$  bromine V. S. which went into combination with the phenol is obtained.

Each cc. of  $\frac{N}{10}$  bromine V. S. represents 0.001563 gm. of pure phenol.

*Example.*—Assuming that 6 cc. of  $\frac{N}{10}$  sodium thio-

sulphate were required to discharge the color of the starch iodide, this deducted from 30 cc. leaves 24 cc., the quantity which combined with the phenol.

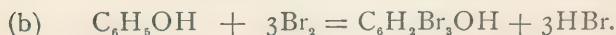
$$0.001563 \times 24 = .037512 \text{ gm.}$$

$$\frac{0.037512 \times 100}{0.039} = 96.1\% \text{ of pure phenol.}$$

The above method originated with Koppeschaar, and is the only volumetric method by which accurate results may be obtained.

It is based upon the fact that bromine reacts with phenol, producing an insoluble precipitate of tribromophenol.

The titration is not made directly; but the phenol solution is treated with an excess of standard bromine solution in the presence of some hydrochloric acid. The hydrochloric acid liberates the bromine, and the freed bromine then reacts with the phenol, as shown by the equations:



$$\begin{array}{r} 6)93.78 \\ 10)15.63 \\ \hline 1.563 \text{ gms.} \end{array} \quad \begin{array}{r} 6)478.56 \\ 10)79.76 \\ \hline 7.976 \text{ gms. or } 1000 \text{ cc. } \frac{\text{N}}{10} \text{ bromine V. S.} \end{array}$$

Thus each cc. of the  $\frac{\text{N}}{10}$  bromine V. S. represents 0.001563 gm. of pure phenol.

The bromine solution which was added in excess, and the liberated bromine of which, is not fixed by phenol, is then found by residual titration with  $\frac{\text{N}}{10}$

sodium thiosulphate V. S. after the addition of some potassium iodide.

The decinormal bromine solution and the decinormal sodium thiosulphate solution being equivalent, each cc. of the latter consumed represents one cc. of the former. Then by subtracting the number of cc. of the sodium thiosulphate solution used from the number of cc. of bromine solution originally added, the quantity of the latter which was actually consumed by the phenol present is found. This number when multiplied by the factor for phenol then gives the quantity of pure phenol present.

The hydrochloric acid used in the above estimation must contain no free chlorine. The potassium iodide must be free from iodate. The starch T.S. should not be added until most of the free iodine has been taken up, and the color of the solution has diminished to light yellow.

The carbolic acid should be diluted with water before titration, and should never be stronger than 0.1 gm. in 25 cc.

Mr. H. Bechurts reports that the precipitate obtained from phenol and bromine is not pure tribromphenol, but a mixture of tribromphenol ( $C_6H_2Br_3OH$ ) and tribromphenol bromide ( $C_6H_2Br_3OBr$ ).

Thus the results obtained by direct titration are often too high, since in the formation of tribromphenol only 6 atoms of bromine are required, while for the production of tribromphenol bromide 8 atoms of bromine are taken up by one molecule of phenol.

The correct results obtained by Koppeschaar's method are attributable to the use of potassium iodide,

which decomposes the tribromphenol bromide, liberating iodine, thus :



The free iodine is then estimated by residual titration, together with that liberated by the excess of bromine added.

Thus the nature of the original precipitate does not affect the final results.

#### ESTIMATION OF PHENOL BY DR. WALLER'S METHOD.

**Solutions Required.**—1. A standard solution of phenol containing 10 gms. of pure phenol in 1 litre.

2. Diluted sulphuric acid of 15% or 20% strength, saturated with alum. This is needed to facilitate the settling of the precipitate.

3. A solution of bromine in water.

**The Estimation.**—Of the sample 10 gms. are introduced into a litre flask, and made up with water to one litre. This solution is filtered through a dry filter, and 10 cc. of the clear filtrate taken for analysis. It is placed into an 8-oz. glass-stoppered bottle, and about 30 cc. of the acid-alum solution added. Into another bottle of the same kind 10 cc. of the standard phenol solution is put, and to this also 30 cc. of the acid-alum solution are added.

The bromine solution is now added from a burette to the bottle containing the standard phenol solution till no more precipitate forms, the bottle being stoppered and well shaken after each addition. The end reaction is further indicated by the appearance of a



yellow color when a slight excess of bromine is reached. Near the end the precipitate forms slowly.

The other solution containing the sample under analysis is titrated in the same way. Then the calculation is made as follows:

The number of cc. of bromine solution consumed by the sample is multiplied by 100, and then divided by the number of cc. of bromine solution used by the standard phenol solution. The answer is the per cent. of pure phenol contained in the sample analyzed.

*The Amount of Water* contained in a solution of carbolic acid may be determined by agitating the solution with an equal volume of chloroform in a graduated cylinder. After standing, the upper layer consists of the water contained in the mixture.

**Crude or Impure Carbolic Acid.**—Phenol in crude carbolic acid is estimated after separating the tarry matters. 20 cc. of the crude carbolic acid are placed in a beaker with 20 cc. of a strong solution of potassium hydrate (sp. gr. about 1.30). The mixture is well shaken and allowed to stand for half an hour; it is then diluted to  $\frac{1}{4}$  litre with water. The tarry matters and other foreign impurities are thus set free, and may be removed by filtration, the filter and contents being washed with lukewarm water till the washings are no longer alkaline. The filtrate and washings are then slightly acidulated with hydrochloric acid, and made up to 3 litres with water.

The small quantity of tarry matters which is left in the filtrate does not interfere in the titration which follows. 50 cc. of this solution are now taken, and 120 cc. of the decinormal bromine V. S. are added, followed by 5 cc. of hydrochloric acid, and the mixture



shaken frequently during half an hour. 10 cc. of potassium iodide T. S. are then added, shaken, allowed to rest (not longer than 5 minutes), and finally titrated with decinormal sodium thiosulphate, using starch T. S. as an indicator.

The number of cc. of the thiosulphate solution used are deducted from 120 cc., the quantity of  $\frac{N}{10}$  bromine V. S. originally added, and the quantity of the latter which was actually taken up by the phenol is obtained. This figure when multiplied by the factor for phenol, 0.001563 gm., gives the quantity of phenol present in the sample operated upon. It must be remembered that the 50 cc. of the diluted carbolic acid used in this assay represent  $\frac{1}{8}$  of one cc. of the original sample.

*Example.*—Let us assume that 80 cc. of decinormal sodium thiosulphate were required in the residual titration. Deducting this from 120 leaves 40 cc. of bromine V. S. which actually went into combination with the phenol; then  $40 \times .001563 = 0.06252$  gm. of phenol present in 0.33 cc. of the solution analyzed.

## CHAPTER XXVI.

## PEPSIN.

PEPSIN, the active constituent of the gastric juice, is an albuminous principle secreted by glands imbedded in the lining membrane of the stomach.

Pepsin has never been isolated in a pure state, and its exact chemical composition is not known, therefore pepsin cannot be quantitatively estimated; but the digestive strength of pepsin or its preparations is measured by the amount of egg-albumen it will digest under certain conditions.

A good pepsin should digest 2000 times its own weight of albumen.

The different tests for ascertaining the digestive power of pepsin do not give the actual strength, but serve to show whether a sample is above, below, or near the standard. All the known tests are comparative tests, and must be conducted under like conditions, as slight variations in the manipulation will frequently occasion very different results even with the same pepsin.

In testing pepsin, it is generally assumed that the sample which will so change the largest amount of egg-albumen as to render it soluble is the best.

Coagulated egg-albumen is not readily soluble, but when acted upon by pepsin it is converted into a substance which is soluble.

The value of pepsin as a digestive agent does not, however, lie in its power to convert albumen into a soluble substance, but rather in the amount of a certain soluble and diffusible principle (peptone) which it produces in a given time and under certain conditions.

The function of the gastric juice in the animal economy consists in reducing the proteids of the food to a condition in which they are easily absorbed into the system, and not reducing them to a soluble condition.

This conversion of the indiffusible proteids into soluble and diffusible peptone does not take place at once, but occurs only after they have passed through several successive stages.

The first step in the digestive action of pepsin upon coagulated egg-albumen is the conversion of the latter into soluble acid-albumen, or syntonin, from which state it is subsequently converted into parapeptone, metapeptene, and finally peptone.

The latter is the only one of these products which is highly diffusible, hence the albumen is not digested until it is converted into peptone.

Thus it is seen that in the tests in which the dissolving power of a pepsin is alone taken into account the actual digestive power is not ascertained.

A weak pepsin may dissolve a large quantity of albumen and convert it into syntonin, but will carry the digestion no further, while a stronger pepsin may in the same time convert the same amount of albumen not only into syntonin, but also into peptone. Apparently both samples have done equal work, the albumen being dissolved in both cases, while in reality one is double the strength of the other.

When pepsin is brought in contact with more albu-

men than it can thoroughly digest, the latter is converted principally into syntonin, and little or no peptone is formed; thus in order to determine the real digestive power of a pepsin, it is necessary to find out how much peptone it produces in a certain period.

This may be accomplished by boiling the solution when the time is up, to prevent further action of the pepsin; the solution is then filtered while still hot, and neutralized with sodium carbonate; the syntonin will then be precipitated.

This precipitate should be dried to a constant weight, and weighed; the difference between this weight and the weight of the albumen originally taken will give approximately the quantity of peptone produced. If, however, the albumen was not completely dissolved, that remaining must also be deducted from the quantity first taken.

It must not be forgotten that the conditions of temperature, acidity, time, amount of agitation, etc., must be the same in all cases.

The U. S. P. method for the valuation of pepsin is as follows:

**Solutions Required.**—(a) To 294 cc. of water add 6 cc. of diluted hydrochloric acid.

(b) In 100 cc. of solution (a) dissolve 0.067 gm. (1 gr.) of the pepsin to be tested.

(c) To 95 cc. of solution (a) brought to a temperature of 40° C. (104° F.) add 5 cc. of solution (b).

The resulting 100 cc. of liquid will contain 0.21 gm. (0.2 cc.) of absolute hydrochloric acid, 0.00335 gm. of the pepsin to be tested, and 98 cc. of water.

Immerse and keep a fresh hen's egg for fifteen minutes in boiling water. Then remove it and place in

cold water. When it is cold, separate the white, coagulated albumen, and rub it through a clean sieve having 30 meshes to the linear inch. Reject the first portion passing through the sieve. Weigh off 10 gms. of the second clean portion, place in a flask of about 200 cc. capacity, and add one half of solution (*c*), and shake to distribute the albumen evenly through the liquid. Then add the other half of solution (*c*) and shake. Place the flask on a water-bath and keep the temperature at about 40° C. (104° F.) for six hours, shaking gently every fifteen minutes. At the expiration of this time the albumen should have disappeared, leaving at most only a few thin, insoluble flakes. The U. S. P. requirement is that the pepsin should be capable of digesting (dissolving) 3000 times its own weight of egg-albumen, coagulated and disintegrated as described above.

The relative proteolytic power of pepsin stronger or weaker than that above described may be determined by ascertaining how much of solution (*b*) made up to 100 cc. with solution (*a*) will be required to exactly dissolve 10 gms. of coagulated and disintegrated albumen under the conditions given above.

This method is somewhat cumbersome and tedious.

The following is Professor Bartley's favorite method. In the hands of the author it has given entirely satisfactory results.

**Solutions Required.**—(*a*) To 25 gms. of the well-mixed whites of several eggs add enough distilled water to make exactly 250 cc. Mix well by thoroughly shaking with clean fine gravel, and boil for 5 minutes. After cooling, make up the solution to the original volume with water. This solution contains

about 10% of egg-albumen, or about 1.22 gms. of the dry albumen in 100 cc.

(*b*) One gm. of the pepsin to be tested is dissolved in 25 cc. of water. 2 cc. of diluted hydrochloric acid (U. S. P.) are added, and enough water to bring the solution up to 50 cc.

**Procedure.**—Measure out into a beaker or bottle 50 cc. of the albumen solution, and warm on a water-bath to about 40° C. (104° F.). Add to this 2 cc. of diluted hydrochloric acid, and from 0.5 to 5.0 cc. of the pepsin solution. The more active the pepsin the less the quantity of the pepsin solution is to be taken. It is sometimes necessary with a pepsin of unknown strength to make a preliminary test, to determine the approximate time required by the digestion, as it is best to so regulate the quantity of pepsin and albumen that the digestion shall be complete in two hours or less. The time when the pepsin is added must be carefully noted, and the temperature kept at about 35° to 40° C. (95° to 104° F.). At intervals of 10 minutes a few drops of the solution are drawn out with an ordinary dropper, and floated upon a few drops of pure nitric acid in a narrow test-tube.

Note the *time* when the nitric acid ceases to give a coagulum of albumen, or when the albumen disappears. We thus get for the calculation the weight of the egg-albumen, *A*; the weight of the pepsin taken, *P*; and the time consumed, *T*. We next assume the standard time of 3 hours, the average time of stomach digestion. The relation between the quantities of albumen and pepsin is expressed by the fraction  $\frac{A}{P}$ ; that is, it is



found by dividing the amount of albumen by the weight of the pepsin.

This result gives the amount of albumen digested by one part of pepsin, in the time observed in the experiment.

To calculate what this would digest in the standard time, we must multiply the above ratio by the ratio of the observed time to the standard time; or, to put this in the form of an equation, we have  $D$  (or digestive power)  $= \frac{A}{P} \times \frac{3}{T}$ .

Suppose 50 cc. of solution (*a*) containing 5 gms. of egg-white be taken, and that 1 cc. of solution (*b*) be taken containing 0.02 gms. of pepsin and that the time required for the digestion is 2 hours.

If we substitute these quantities in the above equation, we have  $D = \frac{5}{.02} \times \frac{3}{2} = \frac{15}{.04} = 375$  gms. That is,

1 gm. of this pepsin is capable of digesting 375 gms. of egg-albumen in 3 hours, or 750 gms. in 6 hours.

As egg-white contains about 12.2 per cent. of dry albumen, 1 gm. of this pepsin will digest 45.7 gms. of dry albumen in 3 hours.

This method gives an exact statement of results, requires little if any skill in manipulation, requires no shaking, and the results are uniform.



## CHAPTER XXVII.

## DETERMINATION OF THE DIASTASIC VALUE OF MALT EXTRACTS AND PANCREATIC EXTRACTS.

A ONE-PER-CENT. solution of starch-mucilage is employed. This is prepared by boiling 10 gms. of pure starch in water, cooling and making up to 1000 cc.

10 cc. of this standard mucilage is mixed in a beaker with 90 cc. of water. The mixture is then warmed to about  $40^{\circ}$  C. ( $104^{\circ}$  F.), and a measured amount of the malt extract or pancreatic extract is added, the exact time of adding it being noted. At short intervals, say every half-minute, a drop of the mixture is placed upon a plate or white slab, with a drop of a dilute aqueous solution of iodine. As long as starch is present in the solution a blue color will be produced when brought in contact with a drop of iodine solution.

When all the starch is converted by the pancreatic extract into erythro-dextrin, the blue color no longer appears and a pink or brown color is produced; when all the erythro-dextrin disappears, no color is produced with the iodine. This is termed the *achromic point*. This point should be reached at the end of not less than six minutes, in order that the end reaction may be determined with sharpness. When it takes longer, the change is too gradual to be exactly determined.

In the statement of results we employ the following formula :

$$D = \frac{S}{P} \times \frac{5}{T}.$$

In this,

$S$  = the weight of the starch employed ;

$P$  = the weight of pancreatic extract or malt extract employed ;

$T$  = the observed time from the addition of the pancreatic or malt extract to the *achromic point* ;

5 = the arbitrarily chosen standard of time in minutes.

*Example.*—10 cc. of starch-mucilage were taken and 0.1 gm. of pancreatic extract was added, and the time required to reach the *achromic point* was three minutes. The above formula would become

$$D = \frac{10}{0.1} \times \frac{5}{3} = \frac{50}{0.3} = 166.66 \text{ cc.}$$

of the starch-mucilage digested by 1 gm. of the extract in five minutes.

As 10 cc. of the solution of starch contains 0.1 gm. of dry starch, 166.66 cc. contain 1.666 gm. This method is equally applicable to malt diastase, salivary diastase, or pancreatic diastase. As malt extract is not official, no standard of strength has been fixed. A good dry extract of malt, however, should digest its own weight of starch in twelve minutes.

Attfield says that 1.5 gm. malt should digest 1 gm. of starch within  $\frac{1}{2}$  hour, with the usual quantity of water, at 60° C.

The following standard of a recent German authority is to be preferred. To 0.6 gm. of starch gelatinized with 60 cc. of water and heated to 40° C. there is

added 0.5 gm. of the extract, dissolved in about 12 cc. of water. No color should be produced by iodine in a drop of the solution, at the end of fifteen minutes. If we substitute these numbers in the above formula, we have

$$\frac{0.6}{0.5} \times \frac{5}{15} = \frac{3.0}{7.5} = 0.4 \text{ gm.};$$

or 1 gm. of a fairly good extract by this test should digest 0.4 gm. of starch in five minutes. This is equivalent to the statement that 1 gm. should digest 1 gm. of starch in twelve minutes.

The method used in the laboratory of Parke Davis & Co. is as follows:

Fill six or more two-ounce vials with two ounces of distilled water and two drops of iodine solution. The iodine solution is prepared from 2 gm. of iodine, 4 gm. potassium iodide, 250 gm. of water.

5 gm. of corn-starch are now mixed with 30 gm. of water, and after thoroughly stirring the mixture, in order to have all the starch in suspension, it is poured into 150 cc. boiling water and the mixture brought to the boiling-point, and the boiling continued for a minute, until all the starch-granules have burst, forming a uniform mucilaginous solution; it is then cooled to 100° F.

5 gm. of malt extract are dissolved in 50 cc. of water. 12½ cc. of this solution, representing 1¼ gm. of malt extract, are added to the starch solution, which is placed on a water-bath, and maintained at a temperature of 100° F. during the test. At the expiration of the first five minutes two drops of the mixture are transferred by means of a nipple pipette to one of the

two-ounce vials containing the iodine. The bottle is shaken and the result noted. This is repeated at intervals of *one minute*, until two drops of the solution no longer produce a blue coloration with the dilute iodine solution, nor more than a faint purple from the formation of intermediate products following the conversion of the starch.

The requirement is that the malt shall convert, according to this test, four times its weight of starch in ten minutes.

## CHAPTER XXVIII.

## ESTIMATION OF ALKALOIDS (VOLUMETRICALLY).

IN making alkaloidal assays of drugs it has long been the custom to evaporate the final ethereal or chloroformic extract, and to weigh the residue as alkaloid. This residue seldom if ever consists of the pure alkaloid, and the amount of impurity is very variable; consequently gravimetric results were in many cases very wide of the truth, and hence unreliable.

The volumetric methods are in most cases much more satisfactory.

While the results of the titration of the *total alkaloids* of drugs cannot be called absolutely accurate, nevertheless experience has shown that they are nearer the truth than those obtained by the gravimetric method.

In estimating an alkaloid by titration, it is essential to know the formula and molecular weight of the alkaloid, as well as the equivalent of acid with which it will combine.

In the case of drugs where two or more alkaloids are present, accurate results can only be obtained by determining how much of each alkaloid is present by a separate assay. But as a rule it is assumed that the alkaloids are present in equal quantities, and the mean of their molecular weights is taken as the basis for the calculation.

If the alkaloid be from a recent extraction, and is in the form of a free alkaloid, it is dissolved in a measured quantity of  $\frac{N}{20}$  hydrochloric-acid solution, and the excess of acid solution then determined by residual titration with  $\frac{N}{20}$  sodium hydroxide solution, using as an indicator a decoction of Brazil wood or some other suitable reagent.

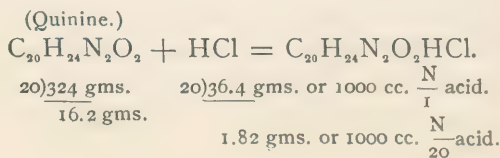
Then by deducting the quantity of the alkali solution used, from the quantity of acid solution first added, the quantity of the latter which combined with the alkaloid is obtained, and from this the quantity of alkaloid present may be calculated.

A molecular weight of a monobasic acid, or half of a molecular weight of a dibasic acid, will combine with and neutralize a molecular weight of an alkaloid, provided the alkaloid is a monacid base.

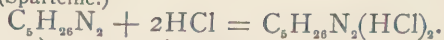
If the alkaloid is a diacid base, one molecular weight will combine with two molecules of a monobasic acid or one molecular weight of a dibasic acid.

Sparteine and Emetine are diacid alkaloids; most of the others are monacid bases.

Thus 1000 cc. of  $\frac{N}{20}$  hydrochloric acid will combine with  $\frac{1}{20}$  of the molecular weight of a monacid alkaloid, or  $\frac{1}{40}$  of the molecular weight of a diacid alkaloid, as the following equations show :



(Sparteine.)



$$\begin{array}{r} 2)114 \\ 2)72.8 \end{array}$$

$$\begin{array}{r} 20)57 \\ 20)36.4 \end{array}$$

$$\frac{2.85 \text{ gms.}}{1.82 \text{ gms. or } 1000 \text{ cc. } \frac{\text{N}}{20} \text{ acid.}}$$

A. H. Allen states: "In titrating an alkaloid with methyl-orange as indicator it is rarely convenient to employ an aqueous solution of the base.

"A solution in proof-spirit can be employed, but the indicator is much less sensitive under such conditions.

"I have found it preferable, especially when an alkaloid is much colored, as is frequently the case in assaying bases directly extracted from their sources, to dissolve the alkaloid in a little chloroform, ether, amyl alcohol, or other suitable *immiscible solvent*.

"The solution is placed in a small stoppered cylinder, together with a few cc. of water colored with a drop or two of methyl-orange. Then on gradually running in the standard acid from a burette, and agitating thoroughly after each addition, it is easy to observe the end of the reaction, as the coloring matter remains in the immiscible layer, and presents a marked contrast to the red color of the aqueous liquid."

Allen has obtained satisfactory results with aconitine and its allies, even when working on as little as 0.030 gm., by using ether as a solvent, and titrating with  $\frac{\text{N}}{50}$  hydrochloric acid.

Prof. P. C. Plugge estimates the alkaloid by titrating the acid of the salt of the alkaloid with standard alkali, and from the result calculates the quantity of alkaloid present. He first determines the uncombined (free) acid by titrating with standard alkali in the presence of litmus.



He then titrates another portion of the solution in the presence of phenolphthalein to determine the total quantity of acid (both free and combined) present, and from this, indirectly, the quantity of alkaloid is calculated.

For the *estimation* of the *alkaloid* in a *commercial salt*, such as quinine sulphate, strychnine sulphate, etc.:

Dissolve the salt in hot water, and titrate with  $\frac{N}{20}$  sodium-hydroxide solution, using phenolphthalein, methyl-orange, or some other suitable indicator.

The acid in combination with the alkaloid acts as though it were a free acid, and may be readily estimated by this method.

Methyl-orange is the best indicator for alkaloids, as it shows an alkaline reaction with most of them.

Phenolphthalein should be used with caution, as an indicator, in titrating morphine, as this alkaloid has a faint acid reaction with it.

It is sometimes preferable to titrate the solution of alkaloidal salt with  $\frac{N}{20}$  NaOH in the presence of phenolphthalein to *exact neutrality*. The alkaloid is now in a free state in a neutral liquid, and may be titrated with  $\frac{N}{20}$  HCl in the presence of methyl-orange.

Prof. Plugge made a number of experiments with a view to determine the possibility of estimating volumetrically, the amount of acid contained in alkaloidal salts, and from this determining the amount of alkaloid. He finds—

(1) That in the salts of the weak opium bases narco-

tine, papaverine, and narceine the amount of acid can be volumetrically estimated with either litmus or phenolphthalein, the reaction being as precise and well defined as if no alkaloid were present.

(2) That in the salts of alkaloids in general, the acid can be readily determined by the use of phenolphthalein, the volatile alkaloids coniine and nicotine being exceptions; and that in the case of morphine, brucine, codeine, and thebaine, phenolphthalein may be used with certain restrictions.

(3) That the *free* acid in solutions of alkaloidal salts can be determined by the use of litmus, but in solutions of weak opium bases litmus cannot be used. The entire quantity of acid, both free and combined, may be determined by the use of phenolphthalein. The difference between the two titrations gives the quantity of acid united to the base.

TABLE SHOWING BEHAVIOR OF SOME OF THE ALKALOIDS  
WITH INDICATORS.

Name.	Formula.	Methyl- orange.	Phenolphthalein	Litmus.
Aconitine .....	$C_{33}H_{45}NO_{12}$	Alkaline	Neutral	Alkaline
Atropine.. .....	$C_{17}H_{23}NO_3$	"	Alkaline	"
Brucine.....	$C_{23}H_{26}N_2O_4$	"	Neutral	"
Cinchona bases..		"	"	"
Cocaine.....	$C_{17}H_{21}NO_4$	"	"	"
Codeine.....	$C_{18}H_{21}NO_3$	"	Alkaline	"
Coniine.....	$C_8H_{15}N$	"	"	"
Morphine.....	$C_{17}H_{19}NO_3$	"	Faintly acid	"
Nicotine.....	$C_6H_7N$	"	Alkaline	"
Quinine .....	$C_{20}H_{24}N_2O_2$	"	Neutral	"
Strychnine .....	$C_{21}H_{22}N_2O_2$	"	"	"

Urea is neutral to methyl-orange, phenolphthalein, and litmus. Caffeine is neutral to phenolphthalein and litmus. Antipyrine is neutral to phenolphthalein and litmus. Pyridine is neutral to phenolphthalein and alkaline to litmus.

TABLE SHOWING THE FACTOR FOR VARIOUS ALKALOIDS WHEN  
TITRATING WITH  $\frac{N}{20}$  ACID OR ALKALI.

Name.	Formula.	Molecular Weight.*	Factor.
Aconitine.....	$C_{33}H_{45}NO_{12}$	647	0.03235
Atropine.....	$C_{17}H_{23}NO_3$	289	0.01445
Brucine.....	$C_{23}H_{26}N_2O_4$	394	0.0197
Cinchonine.....	$C_{19}H_{22}N_2O$	294	0.0147
Cinchonidine.....	$C_{19}H_{22}N_2O$	294	0.0147
Cocaine.....	$C_{17}H_{21}NO_4$	303	0.01515
Codeine.....	$C_{18}H_{21}NO_3$	299	0.01495
Conine.....	$C_8H_{15}N$	125	0.00625
Emetine.....	$\left\{ \begin{array}{l} C_{30}H_{44}N_2O_4 \text{ (Glenard)} \\ C_{30}H_{40}N_2O_6 \text{ (Kunz)} \end{array} \right.$	$\left\{ \begin{array}{l} 496 \\ 508 \end{array} \right.$	$\left\{ \begin{array}{l} 0.0124 \\ 0.0127 \end{array} \right.$
Hyoscyamine.....	$C_{17}H_{21}NO_4$	303	0.01515
Hyoscyamine.....	$C_{16}H_{23}NO_3$	265	0.01325
Morphine.....	$C_{17}H_{19}NO_3$	285	0.01425
Nicotine.....	$C_5H_7N$	81	0.00405
Pilocarpine.....	$C_{11}H_{16}N_2O_2$	208	0.0104
Quinine.....	$C_{20}H_{24}N_2O_2$	324	0.0162
Sparteine.....	$C_{15}H_{26}N_2$	114	0.00285
Strychnine.....	$C_{21}H_{22}N_2O_2$	334	0.0167

## ESTIMATION OF ALKALOIDS BY MAYER'S REAGENT.

The results of titrating with Mayer's solution have only an approximate value, being influenced to a large extent by various conditions, such as degree of dilution, mode of conducting the operation, and the length of time allowed for precipitation after each addition of the reagent.

The Mayer's solution is added from a burette, and the precipitate allowed to subside after each addition until no further precipitation takes place, which can be seen by bringing a drop of the clear supernatant liquid in contact on a watch-glass, with two or three drops of the reagent.

A more common practice is to filter the solution after each addition of the reagent, using the same filter.

When 10 cc. of the filtered liquid are no longer affected by two drops of the reagent, the titration is complete.

If a considerable length of time is allowed to elapse after each addition of reagent, it is found that the results of a titration will coincide more nearly with what theory requires; but the principal advantage which volumetric analysis has over gravimetric, namely, rapidity of execution, is thereby forfeited.

The presence of alcohol, free acetic acid, or ammonia vitiates the result; but gum, albumen, glucose, or extractives in moderate quantities have no effect upon the reaction.

In all comparative titrations with this reagent the dilution of the alkaloidal solution should be the same. The solution should be slightly acid, and its strength about 1-200.

In titrations where the end reaction can only be ascertained by the cessation of the formation of a precipitate, it is often necessary to filter a portion of the turbid solution at intervals during the titration, and test it to see whether the process is completed. In such cases Beale's filter, Fig. 29, may be used. Over the lower end of this instrument a piece of filter-paper is tied, and over that a piece of thin muslin to keep the paper from being broken. When dipped into a turbid mixture the clear liquid rises, and may be poured out of the little spout for testing. If the process is shown to be unfinished, the contents are washed back to the bulk of the liquid, and small portions filtered out at intervals until the process is found to be completed.



FIG. 29.

The **Decinormal Mayer's Solution** is made as follows:

$\frac{N}{10}$  *Mercuric Potassium Iodide V. S., U. S. P.*— $\text{HgI}_2 + 2\text{KI} = 783.98$ . 39.2 gms. in a litre.

Dissolve 13.546 gms. of pure mercuric chloride in 600 cc. of water, and 49.8 gms. of potassium iodide in 100 cc. of water.

Mix the two solutions, and then add enough water to make the mixture measure at or near  $15^\circ \text{C.}$  ( $59^\circ \text{F.}$ ) exactly 1000 cc.

The reaction which takes place when these two solutions are mixed is



A. B. Lyons and many others prefer to use a solution of half the above strength.

Each cc. of the *decinormal solution*, according to Dr. Mayer, precipitates of—

	gm.		gm.		gm.
Aconitine...	0.0267	Coniine. . .	0.00416	Quinidine...	0.0120
Atropine...	0.0145	Morphine..	0.0200	Quinine...	0.0108
Brucine . . .	0.0233	Narcotine..	0.0213	Strychnine..	0.0167
Cinchonine .	0.0102	Nicotine...	0.00405	Veratrine...	0.0269

The precipitates are hydriodates of the alkaloids, respectively, with iodide of mercury; but Lyons finds that they are not of definite composition, though the variation is very slight. This reagent will give similar precipitates with all of the alkaloids, except perhaps colchicine, caffeine, and digitaline.

#### ALKALOIDAL ASSAY BY IMMISCIBLE SOLVENTS.

Many alkaloids are soluble in certain liquids in which their salts are insoluble, while in other liquids the case

is reversed. When such liquids are not miscible the separation may be effected by the so-called "shaking-out process."

In many cases the extraction or separation may be effected by adding to the concentrated aqueous extract, a suitable alkaline precipitant, such as ammonia water or sodium-carbonate solution, which liberates the alkaloid, then shaking up with some solvent, such as chloroform, ether, benzine, benzol, or amyl alcohol. The liberated alkaloid is thus dissolved or washed out of the aqueous solution.

The alkaloid may be again abstracted from this solution by the addition of a dilute acid, which forms again a salt of the alkaloid.

In the U. S. P. chloroform is exclusively used as a solvent for alkaloids.

The extraction is directed to be performed in a glass separator or separatory funnel, which consists of an elongated (globular, cylindrical, or conical) glass vessel, provided with a well-fitting stopper and an outlet-tube containing a well-ground glass stop-cock. (See Fig. 30.)

When the alkaloidal solution, suitably prepared, is introduced into the separator, and the chloroform subsequently added, the latter, owing to its higher specific gravity, will form the lower layer.

If the two are violently shaken together there will often result an emulsion, which will separate slowly, and often imperfectly. This is particularly liable to happen if the aqueous liquid containing the alkaloid, either in solution or suspension, is strongly alkaline, or has a high specific



FIG. 30.



gravity. To avoid this formation of an emulsion it is better to frequently invert the separator or to rotate it rapidly than to shake it violently.

The emulsion may sometimes be destroyed by the addition of more of the solvent, and, if necessary, aided by the application of gentle heat, or by the introduction of a small quantity of alcohol or hot water.

On withdrawing the chloroform solution of an alkaloid from the separator, a small amount of the solution will generally be retained in the outlet-tube by capillary attraction. If this were lost the results of the assay would be seriously vitiated. To avoid this loss, several successive small portions of chloroform should be poured into the separator without agitation, and drawn off through the stop-cock to wash out the outlet-tube.

Another source of loss is due to the pressure generated in the separator by the rise of temperature caused when an alkaline and an acid liquid are shaken together. Some of the liquid adheres to the juncture of the stopper and neck, and when the stopper is loosened some of the liquid is ejected.

When an alkaline carbonate is used instead of caustic alkali for liberating the alkaloid, the liquids should be cautiously and gradually mixed by rotation, and the separator left unstoppered until gas is no longer given off.



## CHAPTER XXIX.

## ESTIMATION OF THE ALKALOIDAL STRENGTH (SCALE SALTS).

FOUR gms. of the scales are dissolved in 30 cc. of water in a capsule with the aid of gentle heat. The solution is cooled and transferred to a glass separator; an aqueous solution of 0.5 gm. of tartaric acid is then added, followed by an excess of solution of sodium hydroxide. The tartaric acid prevents the precipitation of  $\text{Fe}_2(\text{OH})_6$ , and the NaOH sets free the alkaloid. The alkaloid is then extracted by shaking up the mixture with successive portions of chloroform, 15 cc. each time. The chloroformic layers are separated each time and mixed, evaporated in a tared capsule on a water-bath, and the residue dried  $100^\circ \text{C}$ . ( $212^\circ \text{F}$ .), and weighed. Or the residue may be titrated by adding sufficient decinormal sulphuric or hydrochloric acid to dissolve the salts and still remain in excess, then titrating residually with decinormal NaOH or KOH to determine the excess of acid.

## GENERAL METHOD FOR THE ESTIMATION OF THE ALKALOIDAL STRENGTH OF EXTRACTS.

One gm. of the extract is dissolved in 20 cc. of water, heating gently if necessary. 20 cc. of a solution containing 6 gms. of sodium carbonate are added, followed

by 20 cc. of chloroform. Agitate, warm gently, and separate the chloroform. Add to this 20 cc. of dilute sulphuric acid with an equal bulk of water, again agitate, warm, and separate the acid liquor from the chloroform. To this acid liquor add an excess of ammonia, and agitate with 20 cc. of chloroform. When the liquors have separated, transfer the chloroform to a weighed dish, and evaporate over a water-bath. Dry the residue for one hour at  $100^{\circ}$  C. ( $212^{\circ}$  F.), and weigh. This process may be extended to almost any extract containing alkaloids, except opium. If the residue consists of only one alkaloid, the formula and molecular weight of which are known, it may be titrated instead of weighed.

**Assay of Extract of *Nux Vomica*.**—Extract of nux vomica dried at  $100^{\circ}$  C., 2 gms.; alcohol; ammonia-water sp. gr. 0.960, water, chloroform, decinormal sulphuric acid V. S., centinormal potassium hydroxide V. S., of each q. s.

Put 2 gms. of the dried extract of nux vomica into a glass separator. Add to it 20 cc. of a previously prepared mixture of 2 volumes of alcohol, 1 volume of ammonia-water, and 1 volume of water. Shake the separator until the extract is dissolved.

Then add 20 cc. of chloroform and agitate during five minutes. The chloroform dissolves the alkaloids which the ammonia liberated. Allow the chloroformic solution to separate, remove it as far as possible, pour a few cc. more of chloroform into the separator, and without shaking draw this off through the stop-cock to wash the outlet-tube. Repeat the extraction with two further portions of chloroform of 15 cc. each, washing the outlet-tube each time as just directed.

Collect all the chloroformic solutions in a wide beaker; expose the latter to a gentle heat on a water-bath until the chloroform and ammonia are completely dissipated. Add to the residue 10 cc. of decinormal sulphuric acid measured accurately from a burette, stir gently, and then add 20 cc. of hot water. When solution has taken place add 2 cc. of Brazil-wood T. S. (The sulphuric acid combines with the alkaloids, and forms sulphates of the alkaloids.)

Now carefully run into this solution centinormal potassium hydroxide V. S. until a permanent pinkish color is produced, showing a slight excess of the alkali. Divide the number of cc. of centinormal potassium hydroxide used by 10. Subtract the number found from 10 (the 10 cc. of  $\frac{N}{10}$  acid first used), and the number of cc. of the  $\frac{N}{10}$  acid which went into combination with the alkaloids is found.

The two principal alkaloids of nux vomica are strychnine and brucine, and it is assumed that they are present in equal proportions; and thus the factor for total alkaloids is found by taking the mean of their respective molecular weights:

Strychnine, 334	2)728
Brucine, 394	364
728	

364 gms. of the total alkaloids of nux vomica will neutralize 1000 cc. of normal sulphuric acid. 36.4 gms. will neutralize 1000 cc. of decinormal sulphuric acid.

Hence each cc. of decinormal sulphuric acid used in the above assay represents 0.0364 gm. of an equal mixture of strychnine and brucine. And by multi-

plying the number of cc. used by this factor, the quantity of these alkaloids in the 2 gms. of extract taken is obtained, and this quantity multiplied by 50 will give the percentage.

The extract should contain 15 per cent of total alkaloids by the above assay.

*Fluid Extract of Nux Vomica* is evaporated to a solid extract, and then assayed by the above process.

*Tincture of Nux Vomica* is assayed by evaporating 100 cc. to dryness, and the residue then tested by the above process. It should contain 0.3 gm. of alkaloids.

**Assay of Extract of Opium.**—Extract of opium dried at 100° C., 4 gms.; ammonia-water, 2.2 cc.; alcohol, ether, water, of each a sufficient quantity.

Dissolve the extract of opium in 30 cc. of water, filter the solution through a small filter, and wash the filter and residue with water until all soluble matters are extracted, collecting the washings separately. Evaporate in a tared porcelain capsule first the washings to a small volume, then add the first filtrate, and evaporate the whole to a weight of 10 gms. Rotate the concentrated solution about in the capsule until the rings of extract are redissolved. Pour the liquid into a tared flask, and rinse the capsule with a few drops of water at a time until the entire solution weighs 15 gms.

Then add 8.5 cc. of alcohol, shake well, add 20 cc. of ether, and shake again.

Now add the ammonia-water, stopper the flask with a sound cork, shake it thoroughly during ten minutes, and set it aside in a moderately cool place for at least six hours, or overnight.

At the expiration of this time remove the stopper carefully, and brush into the flask any crystals which may adhere to the cork. Place two rapidly acting, plainly folded filters, one within the other, in a small funnel, wet them well with ether, and decant upon the inner one, the ethereal solution, as completely as possible.

Add 10 cc. of ether to the contents of the flask, rotate, and again decant upon the filter; repeat this operation with another 10 cc. of ether. Then pour the liquid in the bottle upon the filter in small portions at a time, in such a way as to transfer the greater portion of the crystals to the filter. When the liquid has passed through transfer the remaining crystals to the filter by rinsing the flask with several small portions of water, using not more than 10 cc. in all.

Apply water to the crystals drop by drop, until they are practically free from mother-liquor, and afterwards wash them with a saturated alcoholic solution of morphine, added drop by drop. When this has all passed through displace the remaining alcohol by ether, using about 10 cc. or more if necessary.

Dry to a constant weight at a temperature not exceeding  $60^{\circ}$  C., and carefully transfer the crystals to a tared watch-glass and weigh them. The weight multiplied by 25 gives the percentage of crystallized morphine present in the extract.

Instead of drying and transferring the crystals to a watch-glass as above directed, the filter containing them may be immersed in some boiling water in a beaker, and an excess of decinormal sulphuric acid added to dissolve the crystals (the quantity being noted); a few drops of methyl orange are then added,

and the mixture titrated with decinormal potassium hydroxide. Deduct the quantity of the latter used from the quantity of decinormal acid first added, and the quantity of decinormal acid which combined with the morphine is found.

1000 cc. of normal acid represents one molecular weight of the alkaloid.

1000 cc. of decinormal acid represents one tenth of a molecular weight of the alkaloid (30.3 gms.); thus each

cc. of  $\frac{N}{10}$  acid represents 0.0303 gm. of crystallized morphine.

The number of cc. used, multiplied by this factor gives the quantity of morphine present in the 4 gms. of extract taken.

This multiplied by 25 gives the per cent. of crystallized morphine; it should contain 18 per cent.

**Assay of Tincture of Opium** (Laudanum).—Tincture of opium, 100 cc.; ammonia-water, 3.5 cc.; alcohol, ether, water, each a sufficient quantity. Evaporate the tincture to about 20 cc., add 40 cc. of water, mix thoroughly, and set the liquid aside for an hour, stirring occasionally and disintegrating the resinous flakes adhering to the capsule; then filter, and wash the filter and residue with water, collecting the washings separately. Evaporate first the washings to a small volume, then add the first filtrate and evaporate to 14 gms. Pour the liquid into a tared flask; rinse the capsule, and add the rinsings until the entire solution weighs 20 gms. Then add 12.2 cc. of alcohol; shake well; add 25 cc. of ether; shake again. Now add the ammonia-water, cork well, shake for ten minutes, and



set aside for at least six hours or overnight, so that the crystals may form.

At the expiration of this time decant the ethereal layer upon a double, plain, rapidly acting filter previously wet with ether; add 10 cc. of ether to the contents of the flask, rotate, and again decant. Repeat this operation with another 10 cc. of ether. Then pour the liquid in the bottle upon the filter, in small portions at a time, so as to transfer the greater portion of the crystals to the filter, and wash the remaining crystals on to the filter with the aid of a small quantity of water, using not more than 10 cc. Then wash the crystals, first with a few drops of water, then with an alcoholic solution of morphine, and finally with ether to displace the alcohol. Dry the crystals to a constant weight and weigh on a tared watch-glass.

If 100 gms. of tincture have been operated upon, the weight of the crystals is at once the per-cent. of crystallized morphine. The yield should be 1.3 to 1.5 gms. of morphine from 100 cc. of tincture.

**Assay of Opium.**—Opium, in any condition to be valued, 10 gms.; ammonia-water, 3.5 cc.; alcohol, ether, water, each a sufficient quantity. Introduce the opium (which, if fresh, should be in very small pieces, and if dry, in very fine powder) into a bottle having a capacity of 300 cc.; add 100 cc. of water; cork well. Agitate the bottle frequently during twelve hours; then pour the whole as evenly as possible upon a wetted filter having a diameter of 12 cm., and when the liquid has drained off wash the residue with water carefully dropped upon the edges of the filter and contents until 150 cc. of filtrate are obtained. Then carefully transfer the moist opium back to the bottle by means of a



spatula, add 50 cc. of water, agitate thoroughly and repeatedly during fifteen minutes, and return the whole to the filter.

When the liquid has drained off, wash the residue as before until the second filtrate measures 150 cc., and finally collect about 20 cc. more of a third filtrate.

Evaporate in a tared capsule, first the second filtrate to a small volume, then add the first filtrate, rinsing the vessel with the third filtrate, and continue the evaporation until the residue weighs 14 gms. From this point proceed exactly as in the assay of tincture of opium.

The weight of the crystals obtained, when multiplied by 10, represents the percentage of crystallized morphine present in the sample of gum. Opium should contain 9%; the powdered not less than 13% nor more than 15%.

**Assay of Cinchona, U. S. P.**—(a) *For Total Alkaloids.*—Cinchona, in No. 80 (or finer) powder and completely dried at 100° C., 20 gms.; alcohol, ammonia-water, chloroform, ether, normal sulphuric acid V. S., potassium hydroxide V. S., each a sufficient quantity. 20 gms. of the cinchona in very fine powder is introduced into a bottle provided with an accurately fitting glass stopper, and to this is added 200 cc. of a previously prepared mixture of 19 volumes of alcohol, 5 volumes of chloroform, and 1 volume of ammonia-water; the bottle is stoppered, and thoroughly and frequently shaken during four hours. The liquid is then passed through a plug of cotton in a funnel into another bottle, being careful that there occurs no loss by evaporation.

100 cc. of the clear filtrate (representing 10 gms. of

cinchona) are transferred to a beaker and evaporated to dryness. The crude alkaloids thus obtained are dissolved in 10 cc. of water and 4 cc. of normal sulphuric acid with the aid of gentle heat. The cooled solution is then filtered into a separator, and the beaker and filter washed with water until the washings no longer have an alkaline reaction, using as little water as possible.

Now add 5 cc. of potassium hydroxide V. S., or sufficient to render the liquid alkaline. The alkaloids are thereby reliberated, and may be shaken out by chloroform. 20 cc. of chloroform are first added, and the extraction repeated, using 10 cc. at a time, until a drop of the last chloroform extraction leaves no residue when evaporated on a watch-glass.

The chloroformic extracts are then mixed, evaporated in a tared beaker, the residue dried at  $100^{\circ}\text{C}$ . ( $212^{\circ}\text{F}$ .), and weighed.

The weight multiplied by 10 will give the percentage of total alkaloids in the specimen tested.

The volumetric method cannot very well be employed here, as the alkaloids exist in varying proportions and are very numerous, thus making it difficult to find a factor which will answer for all cases.

(b) *For Quinine*.—Transfer 50 cc. of the clear filtrate remaining over from the preceding process (and representing 5 gms. of cinchona) to a beaker, evaporate it to dryness, and proceed as directed in the assay for total alkaloids, using, however, only half the amounts of volumetric acid and alkali there directed.

Add the united chloroformic extracts containing the alkaloids in solution, gradually and in small portions at a time, to about 5 gms. of powdered glass contained in

a porcelain capsule placed over a water-bath, so that when the contents of the capsule are dry all or nearly all of the dry alkaloids shall be in intimate admixture with the powdered glass, and the chloroform completely expelled. Now moisten the residue with ether, and having placed a funnel containing a filter (7 cm. in diameter) and well wetted with ether over a small graduated tube (*A*), transfer to the filter the ether-moistened residue from the capsule. Rinse the latter, several times if necessary, with fresh ether, so as to transfer the whole of the residue to the filter; then percolate with ether, drop by drop, until exactly 10 cc. of percolate are obtained. Then collect another 10 cc. by similar slow percolation with ether in a second graduated tube (*B*). Transfer the contents of the tubes to two small tared capsules, properly marked (*A* and *B*), and evaporate to a constant weight at 100° C. (212° F.) and weigh them. (The residue in (*A*) will contain practically all of the quinine, together with a portion of the alkaloid less soluble in ether; the residue in (*B*) will consist almost entirely of these alkaloids.)

From the amount of residue obtained in (*A*) deduct that contained in (*B*). This will give approximately the amount of quinine present in the 5 gms. of sample. Multiply this by 20 and the percentage of quinine containing one molecule of water is obtained.

*Cinchona calisaya* should contain not less than 5 per cent, of total alkaloids, and at least 2.5 per cent, of quinine.

*Cinchona succirubra* should contain not less than 5 per cent, of its peculiar alkaloids.

**Assay of Fluid Extract of Ipecac.**—8 gms. of the fluid extract are diluted with 8 gms. of water in an

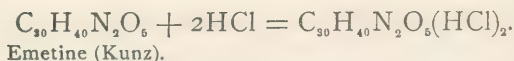
ordinary vial, 32 gms. of chloroform and 48 gms. of ether are added and shaken up; 4 gms. of ammonia water are now introduced, and the mixture frequently agitated during half an hour.

Fifty gms. of the chloroform-ether solution (representing 5 gms. of the fluid extract) are separated, poured into a tared flask, and the solvent distilled or evaporated off; the varnish-like residue is twice treated with 5 to 10 cc. of ether, and evaporated by forcing a current of air into the flask by means of a rubber bulb; the residue is then dried in a water-bath and weighed. For the titration, the residue may be dissolved in a known quantity of decinormal hydrochloric acid; the solution may be assisted by a gentle heat, or the addition of a small quantity of alcohol; 10 or 12 drops of Brazil-wood T. S. are then added and the excess of acid determined by means of decinormal alkali, the latter being added until the liquid becomes cardinal to purplish red in color.

The quantity of decinormal alkali used is then subtracted from the quantity of decinormal acid first added. This gives the quantity of the decinormal acid which was used to neutralize the alkaloids present.

Emetine, according to Kunz, is diacid, and has the formula  $C_{30}H_{40}N_2O_8$ , molecular weight 508. Therefore one molecule of emetine will neutralize two molecules of hydrochloric, or, half a molecular weight, 254 in grammes, will neutralize 1 litre of normal hydrochloric acid, while 25.4 gms. will neutralize 1000 of decinormal acid.

Thus each cc. of decinormal acid represents 0.0254 gm. of emetine. If  $\frac{N}{20}$  acid is used, each cc. represents 0.0127 gm. of emetine.



Emetine (Kunz).

$$\begin{array}{r} 2) 508 \\ 10) 254 \text{ gms.} \end{array} \quad \begin{array}{r} 2) 72.79 \\ 10) 36.37 \text{ gms. or 1000 cc.} \end{array} \quad \frac{\text{N}}{\text{I}} \text{ V. S.}$$

$$\begin{array}{r} 2) 25.4 \text{ gms.} \end{array} \quad \begin{array}{r} 2) 3.637 \text{ gms. or 1000 cc.} \end{array} \quad \frac{\text{N}}{10} \text{ V. S.}$$

$$12.7 \text{ gms.} \quad 1.818 \text{ gms. or 1000 cc.} \quad \frac{\text{N}}{20} \text{ V. S.}$$

Thus if decinormal acid is employed, the number of cc. which were neutralized by the alkaloid when multiplied by .0254 gm. gives the quantity of emetine present in 5 gms. of the fluid extract; and when this is multiplied by 20 the percentage is obtained.

**Assay of Ipecac Root.**—10 gms. of the finely powdered and dried root are placed in a bottle having a capacity of about 150 cc.; 40 gms. of chloroform and 60 gms. of ether are added, and shaken well for several minutes; 10 gms. of ammonia-water are now added; this liberates the emetine, which immediately dissolves in the chloroform and ether, while the suspended powder settles to the bottom of the bottle. The bottle is frequently shaken during one hour, and 5 gms. more of ammonia-water added; the powder then agglutinates in a lump, and the liquid becomes perfectly clear. 50 gms. of the chloroform-ether solution are now taken (representing 5 gms. of the root) and transferred to a tared flask, and the process completed as described under the assay of the fluid extract.

The titration is in this case a little more difficult because of the presence of fat from the root. It is advisable to extract the fat from the root before subjecting it to this assay.

**Estimation of the Strength of Resinous Drugs.**—Take 5 to 10 gms. of the drug in powder, and

place it in a strong glass flask with 100 cc. of pure alcohol (U. S. P. and free from resin). Close the flask with a good cork, and digest it in a warm place at about 49° C. (120° F.) for 12 hours, shaking from time to time. Pour or filter off 80 cc. (representing  $\frac{8}{10}$  of the total drug taken), place it in a weighed beaker, and evaporate to 25 cc. on the top of the water-bath. Now add 50 cc. of distilled water, and boil gently over a low gas flame till all the alcohol is driven off. Let it cool and perfectly settle, pour off the supernatant liquor, wash the deposited resin by decantation with hot distilled water, and then dry the beaker and its contents in the air-bath at 105° C. (220° F.) and weigh, deducting the tare of the beaker. Thus treated, jalap, for example, should show 12 per cent of resin, of which not over 10 per cent should be soluble in ether. Scammony should show 75 per cent resin, which is entirely soluble in ether and in solution of potassa. From the latter it is not reprecipitated by dilute hydrochloric acid in excess. For other resinous drugs no official standard has yet been laid down.



## CHAPTER XXX.

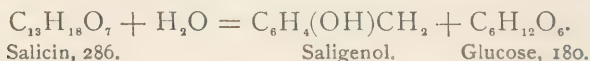
## GLUCOSIDES.

GLUCOSIDES are proximate vegetable principles, which when boiled with a dilute acid, or subjected to some other method of decomposition, take up the elements of water, and yield *glucose* and some other substance, this other substance differing in each case according to the particular glucoside operated upon.

Upon this property of these bodies is based a method for their estimation.

This method depends upon converting the glucoside into glucose, and then estimating the glucose by Fehling's solution in the usual way, and from the amount of glucose formed calculating the quantity of the glucoside.

The conversion of glucosides into glucose is shown by the following equations:

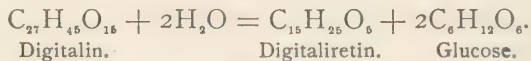


Salicin, 286.

Saligenol.

Glucose, 180.

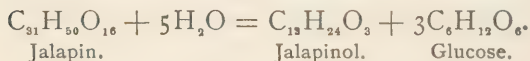
Thus it is seen that 180 gms. of glucose are derived from 286 gms. of salicin.



Digitalin.

### Digitaliretin.

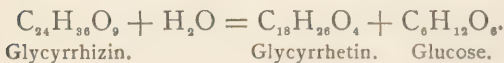
### Glucose.



Jalapin.

Jalapinol.

### Glucose.



### Glycyrrhizin.

Glycyrrhetin.

## Glucose.



## CHAPTER XXXI.

## MILK.

MILK is the nutritive secretion of glands (the mammary glands) which are characteristic of the mammalia.

This secretion takes place as a result of pregnancy and delivery, and continues for a variable period, constituting the entire food of the young animal until it is able to live upon other foods.

The milk of different animals contains qualitatively identical or analogous ingredients to that of the cow, namely, fat (which is held in suspension), nitrogenous matters such as casein and albumen, milk sugar, inorganic salts, and water.

The average composition of cow's milk is as follows :

Fat.....	3.65	per cent.
Proteids .....	4.40	" "
Lactose.....	4.25	" "
Inorganic salts.....	0.75	" "
Total solids.....	13.05	" "
Water .....	86.95	" "
	<hr/>	
	100.00	

In the milk of different animals, however, these ingredients are in different proportions, as the following table shows :

	Human.	Goat.	Mare.	Ass.
	per cent.	per cent.	per cent.	per cent.
Fat.....	3.40	5.2	1.1	1.0
Proteids.....	2.45	3.8	2.2	2.7
Lactose.....	5.75	4.3	5.8	5.3
Inorganic salts.....	0.35	0.7	0.3	0.4
Water.....	88.05	86.0	90.6	90.6
	100.00	100.0	100.0	100.0
Total solids.....	11.95	14.0	9.4	9.4

Milk is a perfect natural emulsion. The casein appears to be the emulsifying agent, a film of which envelops each globule of fat, thus preventing cohesion.

The inorganic salts are chiefly the phosphates of sodium and calcium, and the chlorides of sodium and potassium, but magnesium and iron are also generally present.

The proteids consist mainly of casein with some albumen, the proportion being about as 6 to 1.

Besides the above-mentioned constituents milk also contains a very small quantity of peptone, kreatin, leucin, etc. Also gases, such as  $\text{CO}_2$ , O, and N.

**Colostrum** is the milk secreted in the early stages of lactation; it is rich in proteids, often containing as much as 20 per cent, and contains a few corpuscles of a peculiar character, which look like epithelium-cells, called *colostrum corpuscles*.

**Reaction.**—The reaction of the milk of herbivorous animals is generally alkaline, that of carnivora is generally acid. The reaction of cow's milk is generally neutral, sometimes slightly acid, rarely alkaline.

**Specific Gravity.**—This varies in normal cow's milk from 1.029 to 1.035. It should not be below 1.029.

An excess of fat lowers the specific gravity and the removal of fat raises it. Thus skimmed milk has a higher specific gravity than normal milk.

These facts are made use of for the detection of the ordinary adulterations.

Determinations of the specific gravity of milk should always be made at the temperature of  $60^{\circ}\text{F.}$ , and may be made by any of the ordinary methods. See table of corrections for temperatures other than  $60^{\circ}\text{F.}$ , page 312. A special hydrometer known as the *lactometer* is, however, generally used. The lactometer is graded from  $0^{\circ}$  at the top to  $120^{\circ}$  at the bottom. In taking the specific gravity with this instrument the temperature of the milk must be  $60^{\circ}\text{F.}$

For every  $2\frac{1}{2}^{\circ}$  of temperature above the  $60^{\circ}$  standard, one degree is to be added to the reading of the lactometer; below  $60^{\circ}\text{F.}$  a similar subtraction is to be made.

On the lactometer scale  $0^{\circ} = 1.000$ , the specific gravity of pure water; at  $60^{\circ}\text{F.}$   $100 = 1.029$ , the specific gravity of the poorest possible milk at the same temperature.

If in a sample of milk the lactometer stands at  $80^{\circ}$  the sample contains about 80 per cent of standard milk and 10 per cent of water. If the lactometer stands at  $90^{\circ}$ , the sample contains about 10 per cent of water.

Lactometer Reading.	Specific Gravity.	Lactometer Reading.	Specific Gravity.
0	1.0000	70	1.0203
10	1.0029	80	1.0232
20	1.0058	90	1.0261
30	1.0087	100	1.0290
40	1.0116	110	1.0319
50	1.0145	120	1.0348
60	1.0174		

TABLE FOR CORRECTING THE SPECIFIC GRAVITY OF MILK ACCORDING TO TEMPERATURE.  
(From *Muler's Analytical Chemistry*.)

DIRECTIONS FOR USE.—Find the temperature of the milk in the uppermost horizontal line, and the observed specific gravity in the first and last vertical lines. In the same line with the latter, under the temperature is given the *corrected specific gravity*.  
*Example*.—Supposing the temperature to be 59° and the observed specific gravity 1.032.0, at 60° the specific gravity will be 1.031.9. A specific gravity of 1.032.0 at 66° will be 1.032.9 at 60°.

Observed Specific Gravity.	Degrees of Thermometer ( <i>Fahr.</i> ).																					
	50°	51°	52°	53°	54°	55°	56°	57°	58°	59°	60°	61°	62°	63°	64°	65°	66°	67°	68°	69°	70°	
1.020.0	19.2	19.3	19.4	19.4	19.5	19.6	19.7	19.8	19.9	19.9	1.020.0	20.1	20.2	20.2	20.3	20.4	20.5	20.6	20.7	20.9	21.0	
1.021.0	20.2	20.3	20.3	20.4	20.5	20.6	20.7	20.8	20.9	20.9	1.021.0	21.1	21.2	21.3	21.4	21.5	21.6	21.7	21.8	22.0	22.1	
1.022.0	21.2	21.3	21.3	21.4	21.5	21.6	21.7	21.8	21.9	21.9	1.022.0	22.1	22.2	22.3	22.4	22.5	22.6	22.7	22.8	23.0	23.1	
1.023.0	22.2	22.3	22.3	22.4	22.5	22.6	22.7	22.8	22.8	22.9	1.023.0	23.1	23.2	23.3	23.4	23.5	23.6	23.7	23.8	24.0	24.1	
1.024.0	23.2	23.3	23.3	23.4	23.5	23.6	23.6	23.7	23.8	23.9	1.024.0	24.1	24.2	24.3	24.4	24.5	24.6	24.7	24.9	25.0	25.1	
1.025.0	24.1	24.2	24.3	24.4	24.5	24.6	24.6	24.7	24.8	24.9	1.025.0	25.1	25.2	25.3	25.4	25.5	25.6	25.7	25.9	26.0	26.1	
1.026.0	25.1	25.2	25.2	25.3	25.4	25.5	25.6	25.7	25.8	25.9	1.026.0	26.1	26.2	26.3	26.5	26.6	26.7	26.8	27.0	27.1	27.2	
1.027.0	26.1	26.2	26.2	26.3	26.4	26.5	26.6	26.7	26.8	26.9	1.027.0	27.1	27.3	27.4	27.5	27.6	27.7	27.8	28.0	28.1	28.2	
1.028.0	27.0	27.1	27.2	27.3	27.4	27.5	27.6	27.7	27.8	27.9	1.028.0	28.1	28.3	28.4	28.5	28.6	28.7	28.8	29.0	29.1	29.2	
1.029.0	28.0	28.1	28.2	28.3	28.4	28.5	28.6	28.7	28.8	28.9	1.029.0	29.1	29.3	29.4	29.5	29.6	29.8	29.9	30.1	30.2	30.3	
1.030.0	29.0	29.1	29.2	29.3	29.4	29.5	29.6	29.7	29.8	29.9	1.030.0	30.1	30.3	30.4	30.5	30.7	30.8	30.9	31.1	31.2	31.3	
1.031.0	29.9	30.0	30.1	30.2	30.3	30.4	30.5	30.6	30.8	30.9	1.031.0	31.2	31.3	31.4	31.5	31.7	31.8	32.0	32.2	32.3	32.4	
1.032.0	30.9	31.0	31.1	31.2	31.3	31.4	31.5	31.6	31.7	31.9	1.032.0	32.2	32.3	32.5	32.6	32.7	32.9	33.0	33.2	33.3	33.4	
1.033.0	31.8	31.9	32.0	32.1	32.3	32.4	32.5	32.6	32.7	32.9	1.033.0	33.2	33.3	33.5	33.6	33.8	33.9	34.0	34.2	34.3	34.5	
1.034.0	32.7	32.9	33.0	33.1	33.2	33.3	33.5	33.6	33.7	33.9	1.034.0	34.2	34.3	34.5	34.6	34.8	34.9	35.0	35.2	35.3	35.5	
1.035.0	33.6	33.8	33.9	34.0	34.2	34.3	34.5	34.6	34.7	34.9	1.035.0	35.2	35.3	35.5	35.6	35.8	35.9	36.1	36.2	36.4	36.5	

**The Adulterations of Milk.**—The adulterations usually practised are the abstraction of cream (skimming) or the addition of water, or both. Occasionally the addition of some foreign substance, as sodium carbonate, borax, common salt, or sugar, is met with; or preservatives, as boric or salicylic acids.

The detection of adulterations usually depends upon the determination of the specific gravity, the fat, total solids, and the ash.

These ingredients are, however, present in milk in varying proportions, and hence certain limits of allowable variations have been determined upon from time to time.

The standard adopted in many States in this country is, for specific gravity, not less than 1.029, for total solids, not less than 12 per cent., for fat 3 per cent. The total solids may vary legally from 12 to 13.13 per cent., and the solids not fat, from 8.5 to 9.5 per cent.

**Estimation of Total Solids and Water.**—A small, shallow platinum or porcelain dish about 1½ inches in diameter is heated to redness, allowed to cool, and weighed. About 5 cc. of milk are then put in, and again weighed. The difference between the two weighings gives the weight of the milk taken. Now place the dish on a water-bath and heat until the milk ceases to lose weight. Then cool again and weigh. The weight of the dry residue minus the tare of the dish equals the total solids.

Then by multiplying this by 100, and dividing by the weight of milk taken, the percentage of total solids is found. Thus,

$$\frac{\text{total solids} \times 100}{\text{weight of milk}} = \text{per-cent. of total solids.}$$

This deducted from 100 gives the per-cent. of water.

**Fat.**—Where great accuracy is unnecessary the fat may be determined by treating the total solid residue with successive portions of warm ether until the fat is completely dissolved out. The ethereal solution is then evaporated and the fat which remains behind is weighed, or the residue in the dish may be again weighed. The loss of weight then represents the fat. The results so obtained are 0.3 to 0.5% too low.

*Adams' Method* is the officially recognized method for the accurate estimation of fat in milk.

This consists essentially in spreading the milk over absorbent paper, drying, and extracting the fat. The paper used for this purpose must previously have been thoroughly exhausted with alcohol and ether, and should be in long narrow strips.

The procedure is as follows: 5 cc. of the milk are put into a small beaker and weighed. A strip of the absorbent paper which has been rolled into a coil is thrust into the beaker containing the milk. In a few minutes nearly the whole of the milk will be absorbed; the coil is then withdrawn, and stood dry end down upon a sheet of glass.

It is important to take up the whole of the milk from the beaker, as the paper has a selective action, removing the watery constituents by preference over the fat. The beaker is again weighed, and the milk taken found by difference. The paper charged with the milk is now dried in a water-oven and placed in a Soxhlet extraction apparatus (Fig. 28). About 75 cc. of ether are introduced into the tared flask of the apparatus, and heat applied by means of a



water-bath and continued until exhaustion is complete. The flask is then detached, the ether removed by distillation, and the fat which remains is weighed.

The paper may be charged with the milk by spreading the latter over the surface of the paper by means of a pipette.

*The Werner-Schmid Method.*— This is a satisfactory and at the same time a rapid method for the determination of fat, and is especially suitable for sour milk.

10 cc. of the milk are put into a long tube having a capacity of about 50 cc., and 10 cc. of strong hydrochloric acid are added; or the milk may be weighed in a small beaker and washed into the tube with the acid. The liquids are mixed and boiled for  $1\frac{1}{2}$  minutes, or until the liquid turns dark brown, but not black. The tube and contents are then cooled, and 30 cc. of ether are added, shaken, and allowed to stand until the acid liquid and ether have separated. The cork is now taken out and the wash-bottle arrangement inserted (see Fig. 27). The stopper of this should be of cork, not of rubber, since the ether has a solvent action upon the latter. The lower end of the exit tube is adjusted so as to rest immediately above the junction of the two liquids. The ethereal solution of fat is then blown off, and received in a weighed beaker. Two more portions of 10 cc. each are shaken successively with the acid liquid, blown out, and added to the first. The ethereal solution is then heated on a water-bath, and the residue of fat weighed. The results agree quite closely with the Adams method.

*Calculation Method.*— This rests upon the assumption that every per-cent. of solids not fat, raises the specific gravity by a definite amount, while every per-cent. of



fat lowers it by a definite amount. An accurate determination of the per-cent of total solids and of the specific gravity therefore furnish the necessary data for calculating the amount of fat.

Hehner and Richmond have devised the following formula:

$$F = 0.859T - 0.2186G;$$

in which  $F$  = fat,  $T$  = total solids, and  $G$  = the last two units of the specific gravity and any decimal. Thus if the specific gravity is 1029,  $G$  will be 29; if 1029.5,  $G$  will be 29.5.

*Example.*—Let us assume in the examination of a certain milk that the specific gravity was 1030, and that it contained 12 per cent. of total solids. We then have

$$\text{Fat} = 0.859 \times 12 - 0.2186 \times 30 = 3.75\%$$

When the per-cent. of fat is known, the formula may be transposed so as to calculate the total solids, as follows:

$$T = \frac{F + 0.2186G}{0.859}.$$

*Example.*—A sample of milk is found to contain 3.75 per cent. of fat, and its specific gravity is 1030; then

$$\text{Total solids} = \frac{3.75 + 0.2186 \times 30}{0.859} = 12\%$$

**Ash.**—The ash may be determined by igniting at a dull-red heat the residue left after the fat has been extracted from the total solids. The organic matter is thus all burned off, and the residue is weighed and calculated as ash. The ash should be about 0.75 per cent, never below 0.67.

**To Calculate the Per-cent. of Pure Milk and of**

**Added Water**, the following formula may be adopted, which is based upon the legal standard of the State of New York, which is based upon the poorest possible natural milk, viz., 3 per cent. of fat, 12 per cent. of total solids, and 9 per cent. of "solids not fat."

If, however, a milk has 3 per cent. of fat and only 8.5 per cent. of "solids not fat," it need not be considered as definitely proved to be adulterated.

The quantity of added water should, however, always be calculated upon the average standard of 9 per cent "solids not fat," provided the milk is certainly well below the limit of 8.5 per cent.

The "solids not fat" are used as a basis for the calculation because they are a fairly constant quantity, the fat being variable. The calculation is made thus:

$$\frac{\text{"Solids not fat"} \times 100}{9} = \text{p. c. of pure milk present};$$

and the difference between this result and 100 will of course give the added water.

*Example.*—A sample of milk upon analysis was found to contain 8.1 per cent of solids not fat; then

$$\frac{8.1 \times 100}{9} = \frac{810.0}{9} = 90\%$$

of pure standard milk and 10 per cent of water.

**Total Proteids.**—*Rittenhausen's Copper Process.*—The solutions required are: (1) Copper-sulphate solution, 34.64 gms. in 500 cc.; (2) Sodium-hydroxide solution, 12 gms. to 500 cc.

10 gms. of the milk are diluted to 100 cc. with distilled water and placed in a beaker; 5 cc. of the copper-sulphate solution are now added and thoroughly mixed.

The sodium-hydroxide solution is now added drop by drop, stirring constantly until the precipitate settles quickly, and the liquid is neutral or feebly acid. It should never be alkaline, as an excess of alkali prevents the precipitation of some of the proteids.

The precipitate which includes the fat carries down all of the copper. It is washed by decantation and collected upon a weighed dry filter, the contents of the filter being washed until the total filtrate measures about 250 cc. This filtrate, which contains no copper, is reserved for the determination of the sugar by Fehling's Solution.

The precipitate is washed once by strong alcohol to remove adhering water; it is then washed several times with ether to remove the fat. The residue on the filter, which consists of the proteids and copper hydroxide, is dried at  $265^{\circ}$  F. in the air-bath and weighed. It is then transferred to a porcelain crucible and incinerated, and the residue weighed.

The weight of the filter and contents less the weight of the filter and residue after ignition, gives the weight of the proteids.

**The Milk-sugar** is estimated in the mixed filtrate from the precipitated proteids by the use of Fehling's Solution in the usual way. (See Estimation of Sugar.)

## CHAPTER XXXII.

## BUTTER.

THE composition of commercial butter usually varies within the following limits :

Fat .....	78-94%
Curd ....	1- 3
Water.....	5-14
Salt .....	0- 7

(*Leffmann and Beam.*)

**Reichert's Process** for the detection of foreign fat in butter is undoubtedly the best.

This process is based upon the presence in butter-fat of tributyrin, which yields when appropriately treated an acid (butyric acid), which is relatively much more volatile than the other acids yielded by any of the fats which may be used for the adulteration of butter.

The process is as follows : 2.5 gms. of the butter are melted and filtered into a flask having a capacity of about 150 cc., 20 cc. of a 5-per-cent alcoholic solution of potassium hydrate are added, and the mixture heated to gentle ebullition on a water-bath until the fat is entirely saponified and the alcohol expelled.

The soap, which should form an almost dry mass, not readily detachable from the bottom of the flask by shaking, is dissolved in 50 cc. of water by the aid of

gentle heat. When solution is effected, 20 cc. of dilute sulphuric acid are added. This decomposes the soap and liberates the fat acids.

The flask is then connected with a Liebig's condenser and the contents heated to moderate boiling, a few small pieces of glass, broken clay pipe, or pumice-stone being introduced to prevent bumping.

The distillate, which contains some insoluble acids, is passed through a small wet filter as it drops from the condenser, and is received in a 50-cc. measure.

The distillation is continued until exactly 50 cc. has come over. This distillate contains the volatile and soluble fat acids of the butter examined, and is at once titrated with decinormal sodium-hydroxide solution, using phenolphthalein as an indicator.

When thus treated, pure butter seldom yields less acidity than is represented by 12 cc. of decinormal soda. When butter is made from the milk of a single cow it sometimes falls to 11.5 cc.

Reichert's formula for determining the percentage of butter-fat in mixed fat is

$$B = 7.3(n - 0.3),$$

$n$  being the number of cc. of  $\frac{N}{10}$  alkali used in neutralizing the distillate from 2.5 gms. of the fat.

Oleomargarine requires only 0.8 to 0.9 cc. of alkali for the neutralization of the distillate from 2.5 gms; cacao butter requires 3.7 cc. ; lard, 0.6 cc.

A rapid method for detecting oleomargarine or an admixture of it with butter is to heat the suspected substance in a small tin dish directly over a gas flame. If it melts quietly, foams, and runs over the dish, it is

butter; if it sputters noisily as soon as heated and foams but little, it is oleomargarine.

Another way is to heat the butter for a moment with an alcoholic solution of sodium hydroxide and then empty into cold water. It gives a distinct odor of pineapples (due to ethyl butyrate), while oleomargarine gives only an alcoholic odor.

## CHAPTER XXXIII.

## URINE.

**Normal Urine** when fresh is clear and transparent. Its color is yellowish, reddish, or colorless. It has a peculiar odor, a distinctly acid reaction, and its average specific gravity is from 1018 to 1022.

On standing it generally gives a slight cloud of mucus, which slowly sinks to the bottom; and after heavy exercise or a hearty meal of nitrogenous food, a sediment of urates.

If the urine be very dilute and the temperature is above the mean, decomposition rapidly takes place, and the urine becomes turbid, acquires an alkaline reaction, and develops a nauseous ammoniacal odor.

**Reaction.**—The acid reaction of fresh urine is probably due to the presence of acid phosphate of sodium. If it has an alkaline reaction when first voided it is probably due to the conversion of urea into ammonium carbonate within the bladder; it is then generally turbid, and indicates an abnormal condition.

The reaction is best tested by dropping a small piece of a red and a blue litmus-paper into it. If both are found red in a few minutes the reaction is acid, if both are blue it is alkaline, if both remain unchanged it is neutral.

**Composition.**—The average composition of healthy urine is as follows:



	Per Cent.	Grains per diem.
Water.....	96.00	50 fl. ozs.
Solids as tabulated below.....	4.00	1000 grs.
Urea.....	2.50	500 "
Uric acid.....	0.04	9.5 grs.
Hippuric acid.....	0.075	15.0 "
Creatinine.....	0.075	15.0 "
Pigment, mucus, xanthine, and other extractives .....	0.50	170.0 "
Chlorides of potassium and sodium....	0.50	170.0 "
Sulphates of potassium and calcium...	0.11	40.0 "
Phosphates of potassium and sodium.	0.12	45.0 "
Phosphates of magnesium and calcium.	0.80	35.5 "

Beside these there have been found traces of indican, diastase, glucose, oxalic acid, lactic acid, carbolic acid, and unoxidized sulphur and phosphorus. (From "The Urine;" Holland.)

The composition of urine is not constant: it is influenced by the amount of water and other fluids taken, by the temperature of the skin, by the emotions, the blood-pressure, the amount of work done, the time of day, age, sex, and medicine.

**The Quantity** passed in 24 hours varies considerably. The average quantity passed daily by a healthy adult is 1400 to 1600 cc.—about 50 fl. ozs. The quantity of total solids contained in this is, as seen in the table, about 60 gms., or 1000 grains. About one half of these solids is composed of urea.

In making an analysis of urine the analyst looks for the presence of abnormal constituents, and determines the excess or deficiency of the normal constituents; and therefore, since the composition of urine is not the same at all hours of the day, it is important when accurate results are desired to examine a portion of the total quantity of the urine passed in twenty-four hours. If

this cannot easily be obtained, or only a casual examination is to be made, the first urine passed in the morning may be used.

**Specific Gravity.**—This varies from 1015 to 1028, according to the degree of dilution or concentration. But pathological urine may vary from almost that of water to 1050. The urine of Bright's disease is, as a rule, of low specific gravity, and in diabetes of high specific gravity.

The specific gravity may be taken by any of the usual methods, but the urinometer (a special hydrom-

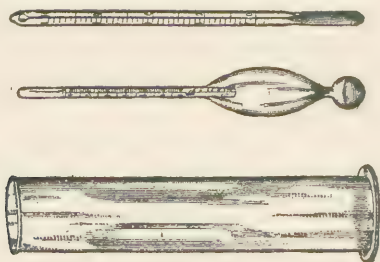


FIG. 31.

eter; see Fig. 31) is generally used for this purpose. This instrument is usually graduated so that only the last two figures of the specific gravity appear upon the stem, and so as to read correctly at 60° F. If the temperature is above 60° F. it will be sufficiently accurate for ordinary clinical purposes to add one degree in specific gravity for every 10 degrees of temperature; that is, if it read 1018 at 80° F., it would read 1020 at 60° F., or for every 1° F. above 60° add 0.0001 to the observed specific gravity. The urinometer is used as follows: Sufficient urine is placed in the upright jar or cylinder to float the urinometer, which is carefully

introduced. When it has come to rest bring the eye on a level with the surface of the liquid in the jar, and take the reading at the lower edge of the meniscus formed by the upper surface of the urine.

The mark on the instrument which is cut by this line, and which can be distinctly seen, is taken as the correct reading.

If the urine be turbid this method cannot be employed.

After taking the specific gravity, reaction, etc., set a portion of the urine aside in a conical glass so as to allow a deposit to form, which must be examined microscopically and chemically, as described later on.

**Total Solids.**—The total solids in urine may be roughly estimated as follows:

The last two figures of the specific gravity when multiplied by the factor 2.33 will give the number of grammes of solid matter in 1000 cc. of the urine.

From this it is easy to calculate the quantity of solids passed in twenty-four hours.

If, for example, 1500 cc. of urine were passed in twenty-four hours, and the specific gravity of this was 1020, the total solids would be  $20 \times 2.33 = 46.6$  gms. in 1000 cc. In 1500 cc. there will be  $\frac{46.6 \times 15}{10} = 69.9$

gms. If it be desired to use the English measures, we may determine the total solids by multiplying the last two figures of the specific gravity by the number of fluid ounces of urine passed, for these last two figures represent approximately the grains of solid matter in a fluid ounce. Thus if 50 fluid ounces were passed and the specific gravity is 1020, the total solids will be  $50 \times 20 = 1000$  grs. in twenty-four hours.

A more exact method of determining the total solids is to evaporate 10 cc. in a white porcelain dish and dry in a water-oven to a constant weight. The difference between the weight of the dish, and of the dish with the solids will be the weight of the solids in 10 cc. of urine. Even by this method there is some loss through volatilization.

**Chlorides.**—For the detection of chlorides a few drops of nitric acid are added to the urine in a test-tube, and then silver-nitrate test solution. A white, curdy precipitate of silver chloride forms, which should occupy not more than one fourth the volume of the urine taken. If it occupies more, the chlorides are said to be increased; if it occupies less space than one fourth, the chlorides are diminished. It is always advisable to compare the specimen under examination with normal urine, subjected to the same test. In most cases such an approximate result is all that is required in a clinical examination.

*The Volumetric Estimation.*—It is sometimes necessary to make a more accurate determination. For this purpose a decinormal solution of silver nitrate is used. 10 cc. of the urine are diluted with about 50 cc. of water; a few drops of potassium chromate T. S. are added, and then the decinormal silver nitrate V. S. run in from a burette until a permanent reddish color is produced. Note the number of cc. of the V. S. used, and multiply this number by the factor for chlorine, 0.00354 gm., the factor for sodium chloride, or 0.00584 gm. This will give the quantity of chlorine or sodium chloride in 10 cc. of urine. This when multiplied by 10 gives the percentage. In highly colored urines this method is sometimes inapplicable, because the change of color is

hidden by the color of the urine. In such cases Volhard's method (see page 112) may be employed.

**Phosphates.**—Phosphoric acid exists in the urine combined with the alkalis and with the alkaline earths. These phosphates are, therefore, generally distinguished by the terms *alkaline* and *earthy* phosphates. By adding an alkali to normal urine the earthy phosphates (calcium and magnesium) are precipitated.

The earthy phosphates may be approximately estimated by adding a few drops of ammonia-water to the urine and observing the amount of turbidity produced after boiling. By comparing this with the amount obtained by the same treatment of normal urine the excess or deficiency is determined. The ppt. is  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{MgNH}_4\text{PO}_4$ .

The alkaline phosphates may be detected in the filtrate from the earthy phosphates by the addition of a few drops of magnesium-sulphate solution and some ammonium chloride. The precipitate will be much more voluminous than that produced by the earthy phosphates, and the excess or deficiency may be determined by comparison with normal urine. The precipitate has the composition  $\text{MgNH}_4\text{PO}_4$ .

The quantitative estimation of the phosphate is rarely required, but may be made by the volumetric process with uranium nitrate.

**Sulphates.**—About 30 grains or 2 grammes of sulphates are daily discharged in the urine.

**Test.**—A few drops of hydrochloric acid are added to the urine in a test-tube to prevent the formation of barium phosphate. Barium chloride T. S. is now added, which causes a white precipitate in the presence of sulphates. This should be compared with results

obtained from equal quantities of healthy urine treated in the same way.

*Volumetric Estimation.*—This is done by the use of a standard solution of barium chloride.

*The Gravimetric Method.*—Take 100 cc. of urine, add 5 cc. HCl and heat to near boiling, then add barium chloride T. S. in slight excess; place the beaker containing the mixture on a water-bath until the precipitate has subsided, decant the clear liquid carefully from the precipitate, add hot water, and when the precipitate has again settled decant again; continue this until the decanted liquid no longer gives a cloudiness with sulphuric acid. Then dry the precipitate and weigh carefully. This gives the quantity of  $\text{BaSO}_4$ , which is precipitated out of the urine by barium chloride.

207.7 parts of barium sulphate represent 98 parts of sulphuric acid. Therefore by multiplying the weight obtained by 98 and dividing by 207.7 the number of grammes of sulphuric acid in the 100 cc. of urine taken is obtained. From these we can easily calculate the quantity eliminated in twenty-four hours.

**Total Acidity.**—Place 50 cc. of the urine in a beaker, add 3 or 4 drops of phenolphthalein, and then run into the beaker carefully from a burette decinormal sodium hydroxide V. S. until a faint permanent red color appears. The number of cc. of the decinormal alkali used multiplied by 0.0063 gives the acidity of 50 cc. of the urine, expressed in grammes of oxalic acid. From this the total acidity is determined by multiplying by the quantity of urine passed in twenty-four hours, and dividing by 50.

If the urine is highly colored the end reaction is



sometimes difficult to see. In such a case the color may be removed by shaking up a portion of the urine with coarsely powdered animal charcoal, then filtering. The urine is thus decolorized, and the pink color produced by the indicator at the completion of the reaction is easily seen.

**Urea**,  $\text{CO}(\text{NH}_2)_2$ .—This is the most important constituent of the urine, as it is the chief condition in which the nitrogen leaves the body. It may be detected by evaporating a few drops of urine on a glass slide, moistening with nitric acid, allowing it to crystallize, and examining the crystals of urea nitrate under a microscope of low power. As urea is generally looked upon as an index of the retrograde changes going on in the body, or of the eliminating power of the kidneys, its quantitative estimation is a matter of great importance.

The quantity of urea eliminated in twenty-four hours has been put as being 30 to 33 gms., or from 430 to 550 grains.

*The Quantitative Estimation of Urea* is effected by treating it with alkaline hypochlorites or hypobromites which decompose the urea into  $\text{CO}_2$ , N, and  $\text{H}_2\text{O}$ .

**Uric Acid**,  $\text{C}_6\text{H}_4\text{N}_4\text{O}_3$ , occurs in urine, sometimes in a free state, but oftener in combination with potassium, sodium, or ammonium, and occasionally with calcium and magnesium. These are called *urates*. It is detected microscopically, and varies in quantity from 0.4 to 0.8 gm. (6 to 12 grs.) in twenty-four hours. The crystals are sometimes large enough to be seen by the naked eye. It deposits, upon standing, in the form of a brick-colored precipitate, commonly called brick-dust.



*Qualitative Chemical Tests.—The Murexid Test.*—A portion of the urine is evaporated to dryness in a porcelain dish upon a water-bath. The residue is then moistened with nitric acid, and after evaporating off the nitric acid the residue is moistened with ammonium hydroxide. If uric acid is present the residue assumes a beautiful purple-red color, due to the formation of murexid.

*The Silver-carbonate Test.*—Make the urine alkaline with  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$ , and moisten a filter paper with the liquid. Now touch the moistened paper with a solution of  $\text{AgNO}_3$ . In the presence of uric acid a distinct gray stain is produced.

*Quantitative Estimation of Uric Acid.*—Acidulate a portion of the urine with  $\text{HCl}$ , and set aside for twenty-four hours. The uric acid is thus set free, and, being insoluble, precipitates and adheres to the bottom and sides of the vessel. It is collected on a weighed filter, washed thoroughly, dried, and weighed. The heat used should not be over  $100^\circ \text{C}$ . ( $212^\circ \text{F}$ ). The weight of the filter and its contents minus the weight of the filter alone gives the weight of uric acid in the volume of urine taken. The quantity eliminated in 24 hours can then be calculated.

#### ABNORMAL CONSTITUENTS.

**Albumen.**—In all cases the urine should be clear before applying the tests for albumen. If not clear, it should be filtered.

(a) *Boiling Test.*—About 10 cc. of the clear urine are placed in a narrow test-tube, one drop of acetic or nitric acid is added, and the tube heated over a small

flame in such a way that the upper portion of the liquid only will be heated. In the presence of albumen the urine will become turbid, more or less so in proportion to the amount of albumen present.

If the acetic or nitric acid is not added before heating, a turbidity will be produced by the phosphates; this, however, will again disappear upon adding the acid.

(b) *The Nitric-acid Test*.—About 2 cc. of pure nitric acid are placed in a test-tube, and the tube being inclined to one side, the urine is carefully run down the side of the tube so that it will float upon and not mix with the acid. An *opaque-white* zone will appear at the line of contact of the two liquids, if albumen is present.

A mixture of nitric acid one volume, and saturated solution of magnesium sulphate five volumes, is sometimes used instead of pure nitric acid in the above test, and is used in the same way.

(c) *Ferrocyanide-of-potassium Test*.—A small portion of the urine is acidulated with acetic acid, and filtered if much of a precipitate forms. This acidulated urine is then floated on a solution of potassium ferrocyanide. A white precipitate appears if albumen is present. This is a very delicate and reliable test; peptone, mucin, or alkaloids are not precipitated by it. This is known as Bödeker's Test.

(d) *Picric-acid Test*.—A cold saturated solution of picric acid may be used in the same way as the nitric acid—by contact. A white zone appears at the line of contact. Alkaloids, mucin, peptones, and urates are, however, precipitated as well as albumen in this

test, and the solution should be heated to redissolve these.

(e) *Sodium-tungstate Test*.—The reagent is made by mixing equal parts of a cold saturated solution of sodium-tungstate and citric-acid solution. This is a very delicate test, and is applied in the same way as the nitric acid and the above. Peptones, alkaloids, mucin, and urates are also precipitated by this reagent, but these are redissolved upon boiling.

(f) *Potassio-mercuric-iodide Test, or Tanret's Test*.—The reagent is prepared as follows: Mercuric chloride, 1.35 gms.; potassium iodide, 3.32 gms.; acetic acid, 20 cc.; distilled water, 80 cc. The two salts are separately dissolved in water, and then the solutions mixed and the acetic acid added. This solution is also used by the contact method. It is very delicate, detecting 1 part of albumen in 20,000 parts of urine. It is necessary to heat in order to dissolve the alkaloids, mucin, and peptone, which are precipitated together with the albumen.

(g) *Acidulated-brine Test*.—The reagent is made by adding one fluid ounce of hydrochloric acid to a pint of a saturated solution of common salt and filtering.

It is used as follows: The solution is heated to boiling, and the urine added by the contact method. A white zone appears at the line of contact if albumen is present. Peptone, alkaloids, etc., are not precipitated by this reagent.

*The Quantitative Estimation* of albumen is of great importance, but comparative tests are, as a rule, sufficient. An easy comparative test is to heat a given quantity of urine in a test-tube, add a few drops of

nitric acid, and set aside for about twelve hours, and then note the volume occupied by the precipitated albumen. This is generally spoken of as *volume per cent.* and has no relation to *actual percentage*.

More accurate results are obtained with Esbach's Albuminometer. This is a graduated glass tube (Fig. 32). Fill the tube to *U* with the urine, then to *R* with the reagent. Close the tube with a rubber stopper, shake, and set aside for 24 hours. Then note the height of the precipitate, as indicated by the graduations. Each of the numbered divisions represents a gramme of albumen in 1000 cc. of urine. The reading should be taken at the middle of the albuminous surface. The reagent: Picric acid, 10 gms.; citric acid, 20 gms.; water, 1000 gms.

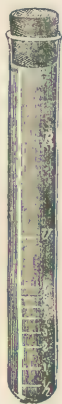


FIG. 32.

**Blood.**—A small quantity of the urine is mixed in a test-tube with an equal volume of a mixture of freshly prepared tincture of guaiac and spirit of turpentine, which has been exposed to the air for some time. If blood-coloring matter is present the mixture assumes an indigo-blue color, the rapidity of formation of which depends upon the amount of blood-coloring matter present. Pus, saliva, and salts of iodine also give a blue color with this test; but it appears only after a considerable lapse of time, and is seldom likely to mislead. Instead of the spirit of turpentine, peroxide of hydrogen may be used.

**Pus.**—The presence of pus is easily revealed by the microscope.

Urine containing pus is always turbid to the naked eye, and deposits a white or greenish-white sediment,

which resembles urates or earthy phosphates. If heated the sediment does not disappear—difference from urates, neither is it dissolved by dilute acids—difference from earthy phosphates. It dissolves, however, in strongly alkaline solutions, giving a gelatinous, ropy liquid. Pus effervesces with hydrogen peroxide.

**Sugar.**—(a) *Bismuth Test*.—A few cc. of urine are placed in a test-tube, and an equal volume of sodium-hydroxide solution and a little bismuth subnitrate; mix well, and boil for a few minutes. A black precipitate is produced if sugar is present.

If albumen is present it must be removed before applying the test, as it is decomposed by boiling with the alkali, forming a black sulphide of bismuth.

(b) *Nylander's Test* is a modification of the above. A solution is made of bismuth subnitrate 2 gms., Rochelle salt 4 gm., sodium hydroxide 8 gms., and distilled water 100 cc.

Heat the urine to boiling, and add a few drops of this alkaline solution of bismuth, continuing the boiling. If sugar is present, the mixture turns black.

This is a very delicate test, but as in the previous one, any albumen must be removed.

(c) *Moore's Test*.—Add one part of liquor soda to two parts of urine, and boil. If sugar is present the urine will become blackish brown. Albumen must be removed before applying the test.

(d) *Picric-acid Test*.—About 5 cc. of the urine are mixed with half as much of picric-acid solution and about 2 cc. of liquor potassa, and boiled. A dark mahogany-red color is developed in the presence of sugar. Albumen will cause turbidity, but will not interfere with the test.

(e) *Trommer's Test*.—5 cc. of urine are mixed in a test-tube with one half of its volume of liquor soda, and one or two drops of a solution of  $\text{CuSO}_4$  (1-10). In the presence of sugar a clear, deep-blue color is obtained. Heat the solution now almost, though not quite, to boiling. At first a greenish then a yellow turbidity forms, which rapidly changes to a reddish-yellow color, and precipitates red cuprous oxide. An excess of the copper solution should not be used.

(f) *Haines' Test*.—The reagent used is a solution of copper sulphate in a mixture of equal parts of glycerine and water.

To about 5 cc. of urine add a few drops of this reagent, and then add sodium-hydroxide solution until the liquid assumes a deep-blue color. The mixture is then gradually heated to boiling. If sugar is present the color changes to yellow, and finally brick-red.

(g) *Indigo-carmin Test*.—The reagent is made by mixing 1 part of dried commercial extract of indigo with 30 parts of pure dry sodium carbonate.

The test: Add enough of this powder to 5 cc. of the urine to give it a transparent-blue color, and heat to boiling. If sugar is present, the color changes to violet, cherry-red, and finally yellow. On gently agitating the tube the colors appear in the reversed order.

(h) *Molisch's Test*.—Put 1 cc. of the urine in a test-tube, add 2 cc. of a saturated solution of alpha-naphthol, mix well, and then add an excess of sulphuric acid. A deep violet color is produced if sugar is present. On dilution with water a blue ppt. occurs.

Thymol or menthol may be used instead of naphthol. The color then produced is deep red.

*Quantitative Estimation*.—This is generally effected



by the use of Fehling's solution. The process is described on page 259.

*By Fermentation.*—This is performed by adding a small quantity of yeast to a certain volume of urine and setting aside for about 24 hours. As the sugar is decomposed the specific gravity of the urine becomes less. Therefore by taking the specific gravity of the urine before and after fermentation a fairly accurate estimation of the sugar present may be made, provided the quantity be not less than 0.5 per cent. Each degree of the urinometer indicates 0.219 per cent. of sugar. If the specific gravity of a sample of urine is found to be 1032, and after subjecting it to fermentation it is 1022, the quantity of sugar present in the sample is 10 times  $0.219 = 2.19\%$ .

**Estimation of Sugar by Dr. Einhorn's Fermentation Saccharometer.**—Take one gramme of commercial compressed yeast (or  $\frac{1}{16}$  of a cake of Fleischmann's yeast), shake thoroughly in the graduated test-tube with 10 cc. of the urine to be examined. Then pour the mixture into the bulb of the saccharometer (Fig. 33). By inclining the apparatus the mixture will easily flow into the cylinder, thereby forcing out the air. Owing to the atmospheric pressure the fluid does not flow back, but remains there.

The apparatus is to be left undisturbed for twenty to twenty-four hours in a room of ordinary temperature.

If the urine contains sugar, the alcoholic fermentation begins in about twenty to thirty minutes. The evolved carbonic-acid gas gathers at the top of the cylinder, forcing the fluid back into the bulb.

On the following day the upper part of the cylinder is filled with carbonic-acid gas. The changed level of



the fluid in the cylinder shows that the reaction has taken place, and indicates by the numbers—to which it corresponds—the approximate quantity of sugar present.

If the urine contains more than one per cent of

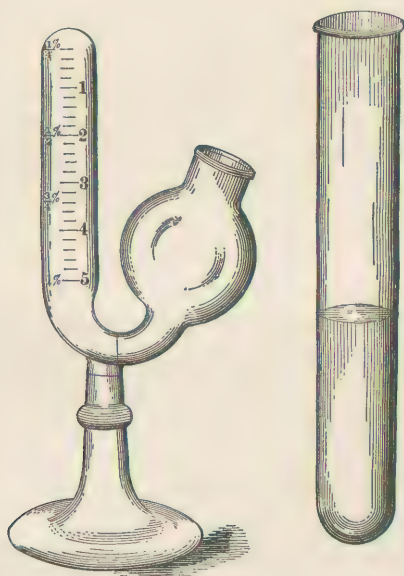


FIG. 33.

sugar, then it must be diluted with water before being tested.

Diabetic urines of straw color and a specific gravity of 1018–1022 may be diluted twice; of 1022–1028, five times; 1028–1038, ten times.

The original (not diluted) urine contains in proportion to the dilution two, five, or ten times more sugar than the diluted urine.

In carrying out the fermentation test it is always recommendable to take, besides the urine to be tested, a normal one, and to make the same fermentation with it.

The mixture of the normal urine with yeast will have on the following day only a small bubble on the top of the cylinder. That proves at once the efficacy and purity of the yeast.

If there is likewise in the suspected urine a small bubble on the top of the cylinder, then *no* sugar is present; but if there is a much larger gas volume, then we are *sure* that the urine contains sugar.

**Test for Bile.**—(a) *Oliver's Test.*—Dissolve 2 gms. of fresh peptone (Savory & Moore's Pulverized), 0.25 gm. salicylic acid, and 2 cc. of 33% acetic acid in water to make 200 cc. The solution should be rendered perfectly clear by filtration.

The urine should also be clarified by filtration, and diluted to a specific gravity of 1008. One cc. of this urine is added to 3 cc. of the above reagent. If biliary salts are present a distinct opalescence at once appears, which becomes more intense in about five minutes. This opalescence will be more or less distinct in proportion to the quantity of bile present.

(b) *Gmelin's Test.*—2 or 3 cc. of partially decomposed yellow nitric acid are placed in a test-tube, and an equal volume of the urine is cautiously poured on top. In the presence of bile pigments a play of colors will appear, beginning with green, then passing through blue, violet, red, and yellow.

The nitric acid may be prepared for this test by adding a fragment of zinc to ordinary nitric acid.

(c) *Pettenkofer's Test.*—Mix equal parts of urine and

sulphuric acid, add one drop of simple syrup, and apply a gentle heat. The color will change from cherry-red to purple if biliary acids are present.

(d) *Ultzmann's Test*.—5 cc. of urine are mixed with 2 cc. of a strong solution of KOH (1-3) and then an excess of pure HCl added. The mixture will become emerald-green if biliary pigments are present.

(e) *Tincture-of-iodine Test*.—A few drops of iodine tincture are floated upon the surface of the urine. If biliary pigments are present, there will appear at the line of contact of the two liquids, after a few minutes, a beautiful emerald-green zone.

## URINARY DEPOSITS.

**Chemical Examination.**—Draw off a portion of the sediment with a pipette or glass tube, and transfer to a watch-glass or small test-tube.

White Deposit.	{	Dissolves on heating urine.....	<i>Ammonium urate.</i>
		Sol. in $\text{NH}_4\text{OH}$ .....	<i>Cystine.</i>
		Insoluble on heating.	Insol. in $\text{NH}_4\text{OH}$ , { Soluble in acetic acid, <i>Earthy Phosphates.</i> Insoluble in acetic acid, <i>Calcium oxalate</i> or <i>oxalurate.</i>
Colored Deposit.	{	Gelatinizes in $\text{NH}_4\text{OH}$ ... <i>Pus</i> (see above).	
		Visibly crystalline (red).....	<i>Uric acid.</i>
		Pale, easily soluble by heat.....	<i>Urates.</i>
		Amorphous. { Deep colored, slowly soluble by heat, <i>Acid urates with uroerythrin.</i> Red, insoluble by heat, alkalies or acids. <i>Blood.</i>	

**Microscopical Examination.**—With a clean pipette draw off a small portion of the sediment, transfer to a clean glass slide, and examine with a  $\frac{1}{2}$ -in. or  $\frac{1}{4}$ -in. objective. A cover glass may be dispensed with.

Deposit is Amor- phous.	{	Small granules with spicules on larger granules.....	{	light = <i>Sodium urate</i> .
		Vanishes on adding KOH or NaOH.....		dark = <i>Ammonium urate</i> .
	{	Permanent, adding KOH or NaOH.....	{	<i>Calcium phosphate</i> (rare).
		Globules, strongly refracting light.....		<i>Fat</i> .
De- posit is Crys- tal- line.	{	Urine Acid.	{	Reddish, cross, or whetstone shape, or in groups..... <i>Uric acid</i> .
				Regular octahedra, envelope-shaped, <i>Calcium oxalate</i> .
	{		{	Hexagonal plates, soluble in $\text{NH}_4\text{OH}$ (white)..... <i>Cystine</i> .
				Bundles of needles crossing each other..... <i>Tyrosin</i> .
	{	Alkaline Urine.	{	Large prisms, soluble in acetic acid (coffin-lid shape), <i>Ammon. magnesium phosphate</i> .
				Brown, double spheres, spiculated, <i>Urate of ammo- nium</i> .
	{		{	Club-shaped crystals, single or in groups, <i>Calcium phosphate</i> .
				Double spheres, radiated structure, soluble in acetic acid, with effervescence, <i>Calcium carbonate</i> (rare).
	{		{	Double spheres, insoluble in acetic acid, <i>Calcium oxalurate</i> (rare).
				Double spheres, yellow or red, radiated..... <i>Uric acid</i> .
Cellu- lar Ele- ments.	{	Red or yellow disks, biconcave ; sometimes irregular in out- line, <i>Blood cells</i> .	{	Granulated corpuscles.
				With dilute acetic acid
	{	show 3 to 5 nuclei.	{	Albumen present..... <i>Pus</i> .
				" absent, <i>Mucus corpuscles</i> .
	{	Round, conical, or flat cells with one nucleus, <i>Epithelium from urinary tract</i> .	{	Round, conical, or flat cells with one nucleus, <i>Epithelium from urinary tract</i> .
				Tadpole-shape, with long tail..... <i>Spermatozoa</i> .
	{	Cylinders, parallel margins, clear, granular, or containing epithelial cells as blood cells... <i>Casts of uriniferous tubules</i> .	{	Cylinders, parallel margins, clear, granular, or containing epithelial cells as blood cells... <i>Casts of uriniferous tubules</i> .
		Fungi, yeast, hairs, threads, etc., etc.... <i>Extraneous matters</i> .		Fungi, yeast, hairs, threads, etc., etc.... <i>Extraneous matters</i> .

—From Bartley's Medical Chemistry.

A little experience in the microscopical examination of urinary sediments will usually enable one to readily recognize the various forms, and thus obviate the necessity for a chemical examination.

**Analysis of Urinary Calculi.**—The following table will show at a glance the compositions and methods of proving the various calculi:

1. *Calculi, fragments of which, heated to redness on platinum, entirely burn away.*

Name.	Physical characters.	Chemical Characters.
Uric acid, $C_5H_4N_4O_3$	Brownish red; smooth or tuberculated; concentric laminæ (common).	Insoluble in water; soluble in KHO by heat, but evolves no $NH_3$ ; dissolves with effervescence in $HNO_3$ and the residue on evaporating the solution is red and gives the <i>mu-raxid</i> test.
Ammonium urate	Clay-colored; usually smooth, and rarely with fine concentric laminæ (uncommon).	Soluble in hot water; soluble in heated KHO, evolving $NH_3$ . Behaves with $HNO_3$ like uric acid.
Cystine, $C_3H_7NSO_2$	Brownish-yellow, semi-transparent and crystalline (very uncommon).	Insoluble in $H_2O$ , alcohol, and ether. Soluble in $NH_4HO$ , and depositing, when allowed to evaporate spontaneously, hexagonal plates. When heated, gives off odor of $CS_2$ .
Xanthin, $C_5H_4N_4O_2$	Pale polished brown surface (very uncommon).	Soluble in KHO; soluble in $HNO_3$ without effervescence, and the solution leaves on evaporation a deep-yellow residue.

2. *Calculi, fragments of which, heated to redness on platinum, do not burn away.*

Name.	Physical Characters	Chemical Characters.
Calcium oxalate, <i>mulberry calculus</i> , $CaC_2O_4$	Deep brown, hard and rough; thick layers (common).	Insoluble in acetic acid, but soluble without effervescence in HCl; heated to redness, it is converted into $CaCO_3$ , which dissolves with effervescence in acetic acid, and the solution gives a white precipitate with $(NH_4)_2C_2O_4$ . Heated strongly before the blowpipe, CaO remains, which, when moistened, is alkaline to test-paper.
Tricalcium phosphate, <i>bone-earth calculus</i> , $Ca_3(PO_4)_2$	Pale brown, with regular laminæ (uncommon).	Infusible before the blowpipe, and residue, when moistened, is not alkaline. Soluble in HCl, and the solution gives a <i>gelatinous</i> precipitate with excess of $NH_4HO$ .
Magnesium ammonium phosphate, <i>triple phosphate calculus</i> , $MgNH_4PO_4$	White, brittle, crystalline, with an uneven and not usually laminated surface (uncommon).	Fusible with difficulty before the blowpipe, evolving $NH_3$ , and residue not alkaline. Soluble in HCl, and solution gives white <i>crystalline</i> precipitate with $NH_4HO$ .
Mixed phosphates of Ca, Mg, and $NH_4$ , <i>fusible calculus</i>	White, and rarely laminated.	Readily fusible before the blowpipe. Soluble in acetic acid, and solution gives a white precipitate with $(NH_4)_2C_2O_4$ , and the filtrate from that precipitate gives a white precipitate with excess of $NH_4HO$ .

## PART III.

### GASOMETRIC ANALYSIS.

#### CHAPTER XXXIV.

##### THE NITROMETER.

FOR general gas analysis, and for the rapid estimation of such substances as ethyl nitrite, hydrogen peroxide, urea, bleaching-powder, manganese peroxide, etc., an instrument called the *nitrometer* is used.

The apparatus in its simplest form is shown in Fig.

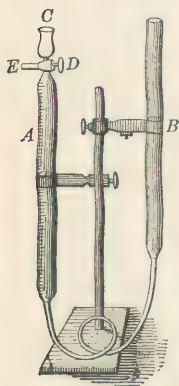


FIG. 34.

34. It consists of a measuring-tube (*A*) graduated in cc., and fitted at the top with a three-way stop-cock (*D*) and a glass cup or funnel (*C*). The stop-cock is so arranged that according to the way in which it is turned it will discharge the contents of the cup either into the tube below or out in the waste-opening (*E*); or it will discharge the contents of the graduated tube into the waste-opening.

The graduated tube generally has a capacity of 50 cc., and is graduated in  $\frac{1}{10}$  cc., the graduation beginning at the top. This measuring-tube is connected by means of a strong



flexible india-rubber tube with an ungraduated tube (*B*) called the control-tube, pressure-tube, or level-tube. Both tubes are held in clamps upon a stand.

With this apparatus gases can be rapidly and accurately measured at definite temperature and pressure.

In measuring the gas the instrument is filled with some liquid in which the gas is insoluble—generally mercury. In many cases a saturated solution of salt may be used.

Suppose we fill the instrument with mercury in such quantity that when the stop-cock is opened and the control-tube raised, the mercury will rise as far as the top, and about two inches in the control-tube.

The top is now closed, the control-tube lowered, and a little carbonic-acid gas admitted through (*E*). The top is then again closed, and the instrument allowed to stand until its contents have acquired the temperature of the room. A centigrade thermometer suspended to the stand will then give the temperature of the gas.

The control-tube is now raised or lowered so as to make the level of the liquid in both tubes the same. This makes the pressure in the tube the same as the atmospheric pressure outside, and by referring to a barometer standing near this pressure is ascertained.

We now have a definite volume of the gas at a known temperature and pressure.

It now only remains to read off the volume of the gas, and correct it to the normal temperature and pressure by Charles' and Boyle's laws, respectively.

The normal temperature and pressure is  $0^{\circ}$  C. and 760 mm. pressure.

The weight of the gas in grammes may then be cal-



culated from its volume by multiplying the number of cc. at the normal temperature and pressure, by the weight of one cc. of the gas in grammes.

This weight may be found as follows:

1000 cc. of hydrogen at normal temperature and pressure weigh 0.0896 gm. One cc. of H then weighs 0.0000896 gm.

One cc. of oxygen weighs 16 times as much, and one cc. of nitrogen weighs 14 times as much. Therefore, by multiplying the weight of one cc. of H by the atomic weight of an elementary gas, or half the molecular weight of a compound gas, the weight of one cc. of that gas is obtained.

According to the law of Charles, *the volume of a gas under constant pressure varies directly with the absolute temperature.*

All gases expand or contract by  $\frac{1}{273}$  of their volume for each centigrade degree of temperature, increased or decreased.

We may regard a gas at  $0^{\circ}$  C. as having passed through  $273^{\circ}$  C. In other words,  $273^{\circ}$  below zero must be regarded as the absolute zero, and  $0^{\circ}$  C. as  $273^{\circ}$  absolute temperature.

Thus the absolute temperature centigrade is the observed temperature  $+ 273^{\circ}$ .

*Example.*—A given volume of oxygen gas at  $15^{\circ}$  C. measures 20 cc. What will it measure at  $0^{\circ}$  C.?

$$\frac{0^{\circ} + 273^{\circ} \times 20}{15^{\circ} + 273^{\circ}} \quad \text{or} \quad \frac{273^{\circ} \times 20}{288^{\circ}} = 18.95 \text{ cc.} \quad \text{Ans.}$$

**Boyle's Law.**—The volume of a confined gas is inversely proportional to the pressure brought to bear upon it. That is, the less the pressure the greater the volume, and *vice versa*.

*Rule.*—Multiply the observed volume by the observed pressure, and divide by the normal pressure.

*Example.*—A given volume of gas at 750 mm. pressure measures 20 cc. What will it measure at 760 mm. (the normal pressure)?

$$\frac{750 \times 20 \text{ cc.}}{760} = 19.73 \text{ cc.} \quad \text{Ans.}$$

Now let us take an example in which both laws are involved.

A given volume of oxygen at 15° C. subjected to a pressure of 750 mm. measures 20 cc. What will it measure at the normal temperature and pressure?—i.e., 0° C. and 760 mm.

In the first example we find that 20 cc. of oxygen at 15° C. will measure at 0° C. 18.95 cc. Then

$$\frac{750 \times 18.95 \text{ cc.}}{760} = 18.70 \text{ cc.} \quad \text{Ans.}$$

Now to find the weight of this volume of oxygen we proceed as follows:

1 cc. of H weighs 0.0000896 gm. ;

1 cc. of O weighs  $16 \times .0000896 = 0.0014336$  gm. ;

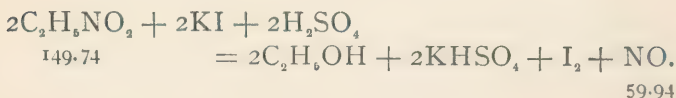
18.70 cc. of O =  $18.70 \times 0.0014336$  gm., or 0.02680832 gm.

## CHAPTER XXXV.

## ASSAY OF SPIRITUS ÆTHERIS NITROSI.

**Spirit of Nitrous Ether.**—This is an alcoholic solution of ethyl nitrite ( $C_2H_5NO_2 = 74.97$ ), yielding when freshly prepared and tested in the nitrometer not less than 11 times its own volume of nitrogen dioxide ( $NO = 29.97$ ), U. S. P.

When nitrites are mixed with an excess of KI and acidulated with  $H_2SO_4$ , iodine is liberated, and all the nitrogen of the nitrite is evolved in the form of NO, as shown in the equation



The process of the U. S. P. is conducted as follows:

Open the stop-cock of the measuring-tube, raise the control-tube, and pour into the latter a saturated solution of NaCl until the measuring-tube, including the bore of the stop-cock, is completely filled. Then close the stop-cock and fix the control-tube at a lower level. Now introduce into the funnel at the top of the measuring-tube 5 cc. of recently prepared spirit of nitrous ether, open the stop-cock, and allow the spirit to run into the nitrometer, being careful that no air enters at

the same time. 10 cc. of potassium iodide T. S. are now added in the same manner, and followed by 10 cc. of normal sulphuric acid V. S. Effervescence takes place immediately, and if the tube be vigorously shaken at intervals the reaction will complete itself in ten minutes. The control-tube is now lowered so as to make the level of the liquid in both tubes the same, and the volume of the gas in the graduated tube read off.

According to the U. S. P., the volume of NO generated at the ordinary indoor temperature (assumed to be at or near  $25^{\circ}\text{C.}$ ,  $77^{\circ}\text{F.}$ ) should not be less than 55 cc. if 5 cc. of the spirit are taken, corresponding to about 4 per cent. of pure ethyl nitrite.

Sodium-chloride solution is used in the above assay, because owing to its density the spirit will float on top, and the gas evolved will not dissolve in it. At the same time the expense of using mercury is saved. It is important that no air be allowed to get into the measuring-tube, because this would convert the NO into a higher oxide of nitrogen, which would dissolve in the salt solution, and thus vitiate the result.

If it is desired to ascertain the percentage of ethyl nitrite present in a sample of spirit of nitrous ether which is either above or below the U. S. P. standard, it is necessary to find how much ethyl nitrite each cc. of NO represents, under a definite degree of temperature and pressure.

It is generally convenient to correct the volume of gas evolved at higher temperatures to its corresponding volume at  $0^{\circ}\text{C.}$

The calculations involved are fully explained below.

*Example.*—5 cc. of spirit of nitrous ether (sp. gr. 0.840)

are treated in a nitrometer, and the NO evolved measures 55 cc.

The temperature at which the operation is conducted is 25° C., and the atmospheric pressure normal.

What per-cent. of ethyl nitrite is present in the sample?

By consulting the equation given above, it will be seen that one molecular weight of NO = 29.97 is evolved from one molecular weight of ethyl nitrite, 74.87.

Now reduce the volume of the gas liberated at 25° C. to its corresponding volume at 0° C. Thus

$$273^{\circ} + 25^{\circ} : 55 :: 273^{\circ} + 0^{\circ} : x. \quad x = 50.4 \text{ cc.}$$

Thus the gas evolved from 5 cc. of the spiritus ætheris nitrosi, measured at 0° C., is 50.4 cc.

The next step in the calculation is to find how much ethyl nitrite each cc. of the evolved NO represents. One litre of hydrogen at 0° C. and normal pressure weighs 0.0896 gm.

By multiplying this weight by half the molecular weight of NO, the weight of 1000 cc. of the latter gas is obtained; this will be found to be 1.3423. Now if 1.3423 gm. of NO measures 1000 cc., 29.97 gms. will measure 22328.24 cc.

$$1.3423 : 1000 :: 29.97 : x. \quad x = 22328.24.$$

Then if 22328.24 cc. of NO are evolved by, and consequently represent, 74.87 gms. of ethyl nitrite, as the equation shows, 1 cc. of NO will represent 0.0033529 gm. of pure ethyl nitrite.

Now, since in the above example 50.4 cc. of gas were

evolved at  $0^{\circ}\text{C.}$ , the 5 cc. of spirit of nitrous ether examined must contain

$$50.4 \times 0.0033529 \text{ gm.} = 0.1689912 \text{ gm.}$$

of pure ethyl nitrite.

In order to determine the percentage strength, the weight of the spirit taken must be known. This may be found by multiplying the measure by the specific gravity, 5 cc.  $\times$  0.840 = 4.2 gms. Then

$$4.2 \text{ gms.} : 0.1689912 \text{ gm.} :: 100 : x. \quad x = 4\%.$$

$$1 \text{ litre of NO } \left\{ \begin{array}{l} \text{at } 0^{\circ}\text{C., and 760 mm.} = 1.3423 \text{ gms.,} \\ \text{at } 25^{\circ}\text{C., and 760 mm.} = 1.2297 \text{ gms.} \end{array} \right.$$

1 cc. of NO is the equivalent of—

	At $0^{\circ}\text{C.}$	At $25^{\circ}\text{C.}$
Amyl nitrite, $\text{C}_5\text{H}_{11}\text{NO}_2$ ...	0.0052305	0.0047923 gm.
Ethyl nitrite, $\text{C}_2\text{H}_5\text{NO}_2$ ...	0.0033529	0.0030716 "
Sodium nitrite, $\text{NaNO}_2$ ...	0.0030873	0.0028283 "

**Amyl Nitrite** is a liquid containing about 80 per cent. of amyl nitrite (principally iso - amyl nitrite),  $\text{C}_5\text{H}_{11}\text{NO}_2 = 116.78$ , together with variable quantities of undetermined compounds.

The U. S. P. assay is as follows: 0.26 gm. of amyl nitrite are diluted with 5 cc. of alcohol, introduced into the nitrometer as directed for spiritus ætheris nitrosi;

10 cc. of potassium iodide T. S. and 10 cc. of  $\frac{\text{N}}{1} \text{H}_2\text{SO}_4$

V. S. are then added; and the volume of NO generated, measured at the ordinary indoor temperature (assumed to be at or near  $25^{\circ}\text{C.}$  or  $77^{\circ}\text{F.}$ ), should be about 40 cc. Each cc. at this temperature represents 0.004792 gm. of pure amyl nitrite, or about 2 per cent.





Thus each molecule of the nitrate radical  $\text{NO}_3$  gives off a molecule of  $\text{NO}$ .

Not more than 0.2 gm. of nitrate should be taken for analysis, since, if this quantity is exceeded, the volume of gas evolved will be greater than the instrument can conveniently hold. In this estimation the nitrometer is filled with mercury instead of brine; the nitrate is dissolved in 5 cc. of water, introduced into the nitrometer, and followed by excess of strong sulphuric acid. The instrument is well shaken for some time, and when action has ceased and the contents have cooled down to the temperature of the room, the level is adjusted and the volume of  $\text{NO}$  read off and calculated in the usual way.

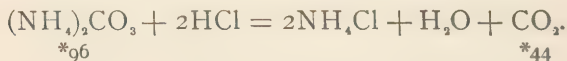
## CHAPTER XXXVI.

ESTIMATION OF SOLUBLE CARBONATES BY THE  
USE OF THE NITROMETER.

THE nitrometer may be used for estimating ammonium carbonate in aromatic spirit of ammonia.

The nitrometer in this case must be charged with mercury, as the liberated  $\text{CO}_2$  is soluble in aqueous liquids.

A given volume of the spirit is introduced into the nitrometer, followed by an excess of dilute  $\text{HCl}$ , and the evolved gas then read off; and from its quantity the proportion of ammonium carbonate may be calculated by applying the equation



The volume of gas liberated must first be reduced to its corresponding volume at  $0^\circ \text{C}$ .

Each cc. of  $\text{CO}_2$  at  $0^\circ \text{C}$ . weighs 0.001966 gm. Now if 44 gms. of  $\text{CO}_2$  represent 96 gms. of normal ammonium carbonate, how much ammonium carbonate does 0.001966 gm. of  $\text{CO}_2$  represent?

$$44 : 96 :: 0.001966 : x. \quad x = 0.004289 \text{ gm.}$$

Thus each cc. of  $\text{CO}_2$  at normal pressure and  $0^\circ \text{C}$ . represents 0.004289 gm. of  $(\text{NH}_4)_2\text{CO}_3$ , approximately.

## CHAPTER XXXVII.

## ESTIMATION OF UREA IN URINE.

THIS determination is based upon the fact that when urea is decomposed by an alkaline hypochlorite or hypobromite, carbon dioxide and nitrogen are given off, as the equation shows:



The liberated N may be measured, and from its quantity the quantity of urea calculated; the other products of the decomposition go into solution.

The hypobromite solution is prepared as follows: 100 gms. NaOH are dissolved in 250 cc. of water, and when this solution has become cold 25 cc. of bromine are added, and the solution kept cold. This solution contains sodium hypobromite, bromate, and hydroxide; it readily undergoes decomposition, and should therefore always be freshly prepared when wanted for use.

The solution of sodium hypochlorite is generally preferred to the hypobromite, because it is more stable, just as efficacious, and the disagreeable handling of bromine is obviated.

Various forms of apparatus have been devised for the quantitative estimation of urea.

The simplest of these is probably the one devised by Dr. Chas. A. Doremus. (See Fig. 35.)

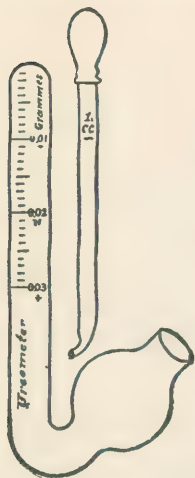


FIG. 35.

The long arm of the *ureometer* is filled with the hypobromite solution, and then 1 cc. of the urine is introduced by the aid of the pipette. The pipette is introduced through the bulb as far as it will go in the bend, and the nipple is then gently but steadily compressed, being careful that no air is admitted.

The volume of the liberated gas is read off after the froth has subsided.

The ureometer indicates, according to its graduation, either milligrammes of urea in 1 cc. or grains of urea per fluid ounce of urine.

It also indicates by the signs +, N, and - whether the urea is present in an increased, normal, or decreased quantity.

*Another Convenient Form of Apparatus* is a tube closed at one end, and graduated so that each division indicates a grain of urea in a fluid ounce of urine, when 1 cc. of urine is taken for the estimation. (See Fig. 36.)

The process is conducted as follows: A 25-per-cent. solution of KBr is introduced to the fifth division. The chlorinated-soda solution is then added to the fifteenth or twentieth division. The tube is now inclined, and pure water carefully poured upon the liquid so that it will float on top; 1 cc. of urine is then added carefully, so that it will not mix with the reagents below, but remain in the water at the surface of the fluid. The open end of the tube is then

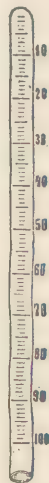


FIG. 36.

quickly closed with the thumb, and the top firmly grasped in the right hand. The tube is then inverted, and the contents well mixed. The decomposition which takes place is usually ended in five minutes. As soon as the effervescence has ceased, the reading is taken at the surface of the liquid. The tube is now opened under water, when the column of fluid in the tube will fall; the reading is then again taken. The difference between the two readings gives the number of grains of urea in a fluid ounce of the urine.

*Squibb's Urea Apparatus* (Fig. 37) is a very simple apparatus, and can be easily improvised in a drug-store. It consists of two wide-mouthed bottles, the larger of which (*C*), capable of holding about 250 cc., is fitted with a rubber stopper, through which is passed a curved

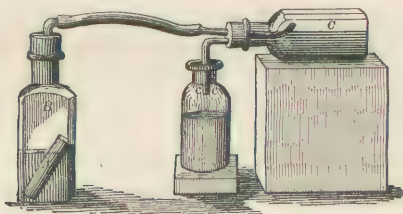


FIG. 37.

delivery-tube and a short straight tube, the latter connected by a piece of rubber tubing to the short glass tube in the rubber stopper of the smaller bottle or generating-bottle (*B*). In the generating-bottle is a small test-tube (*A*).

Into the test-tube *C* is placed 5 cc. of urine, and into the smaller bottle *B* is put 20 cc. of the hypobromite solution, or strong liquor sodæ chlorinatæ. The test-tube is then placed in the generating-bottle *B*, being careful that the urine and the reagent do not come in contact. The larger bottle *A* is now filled with water

and the two bottles connected by the rubber tube, the larger bottle being placed on its side upon a block, and when all connections are tight, the generating-bottle is shaken so that the urine will mix with the reagent.

Decomposition takes place, and the generated gas passes into the bottle *C*, displacing water, which is caught in a graduated cylinder or other measuring vessel. The volume of water displaced is equivalent to the volume of gas evolved.

Each cc. of nitrogen gas evolved at 0° C. and normal pressure represents 0.0027 gm. of urea. Then by multiplying the number of cc. evolved by this number the quantity of urea in the 5 cc. of urine taken is ascertained.

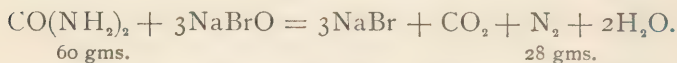
The volume of gas obtained when the operation is conducted at ordinary temperatures should always be reduced to its corresponding volume at 0° C. and 760 mm.

The factor 0.0027 is found in the following manner:

1000 cc. of H at 0° C. weigh 0.0896 gm.;

1000 cc. of N at 0° C. weigh 1.2544 gms.

By the equation it is seen that 60 gms. of urea evolve when decomposed 28 gms. of N.



Now we will find the volume occupied by 28 gms. of N at 0° C.

$$1.2544 \text{ gms. of N} = 1000 \text{ cc.}$$

$$\begin{array}{ccccccc} \text{gms.} & & \text{cc.} & & \text{gms.} & & \text{cc.} \\ 1.2544 & : & 1000 & :: & 28 & : & x. \quad x = 22321.43 \text{ cc.} \end{array}$$

Thus 60 gms. of urea evolve 22321.43 cc. of N; 1 cc. of N thus represents 0.0027 gm. of urea,

## CHAPTER XXXVII.

## HYDROGEN DIOXIDE

As stated in a previous chapter, hydrogen dioxide when acted upon by an acidulated solution of potassium permanganate, is decomposed and oxygen is evolved. One half of this oxygen comes from the dioxide and the other half from the permanganate.

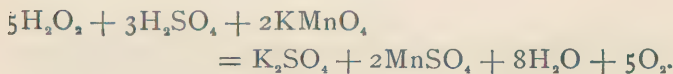
Therefore if 1 cc. of the dioxide be treated in this way and 20 cc. of oxygen are evolved, the strength of the solution is 10 volumes.

The nitrometer may be used for this estimation.

This instrument is charged with a concentrated solution of sodium sulphate (which in this case is better than brine), and 1 cc. of the dioxide introduced from the funnel, followed by excess of solution of permanganate acidulated with sulphuric acid.

This latter solution should be of such strength that when the reaction is completed, the solution should still have a purple color.

The reaction is thus illustrated:



By the use of *Squibb's Urea Apparatus* the estimation may be easily and rapidly made.

Into the generating-bottle is put about 30 cc. of a



strong, acidulated solution of potassium permanganate, and a small test-tube containing 1 cc. of  $\text{H}_2\text{O}_2$  is carefully introduced. The two liquids must not be allowed to come in contact.

The larger flask is filled with water or, better, a solution of sodium sulphate, the connection is then made by means of the rubber tube, and the generating-bottle tipped over and agitated so that the liquids will mix and the reaction take place.

The liberated oxygen then passes into the larger bottle, displacing an equal volume of water, which is collected and measured. Half of this volume represents the volume strength of the  $\text{H}_2\text{O}_2$ .

*An Improvised Nitrometer* may be used. The author has found the following instrument convenient :

To the bottom of an ordinary 50-cc. burette is attached a suitable length of rubber tubing, to the other end of which is attached another burette or *ungraduated* tube, which serves as a control-tube.

Into the top of the burette is fitted a rubber stopper, through which passes a short glass tube, which is connected by means of a rubber tube to a generating-bottle similar to that used with *Squibb's Urea Apparatus*. Into the control-tube is poured the solution of sodium sulphate, sufficient to fill the burette to the zero-mark and have the surface of the liquid in both tubes on a level.

About 30 cc. of strong permanganate solution acidulated with sulphuric acid are now placed in the generating-bottle, and then the small test-tube or homopathic vial, containing exactly 1 cc. of hydrogen dioxide, is placed in. The generating-bottle is then stoppered and agitated, the evolved gas passes over, and

forces the liquid in the burette, down. The control-tube is then lowered so as to bring the surfaces of the liquid in both tubes on a level.

The reading is then taken.

Each cc. of gas represents  $\frac{1}{2}$  volume of oxygen evolved from the peroxide if 1 cc. of the latter is used. Each cc. of oxygen evolved from 1 cc. of the peroxide represents also 0.001696 gm. of absolute  $\text{H}_2\text{O}_2$ , or 0.0008 gm. of available oxygen.

Thus if from 1 cc. of the solution of hydrogen peroxide, 20 cc. of gas are evolved, it is a so-called 10-volume solution, and contains  $.001696 \times 20 = 0.03392$  gm. of absolute  $\text{H}_2\text{O}_2$ , or  $0.0008 \times 20 = 0.016$  gm. of available oxygen.

## APPENDIX.

## INDICATORS.

ACCORDING to R. A. Cripps, the requirements of a good indicator are :

I. The end reaction should be marked by a prominent change of color.

II. The smallest possible quantity of the reagent should be required to effect this change.

III. High tinctorial power, which of itself assists in the fulfilment of the second requirement, less of the indicator being required.

IV. The change of color should not be effected by the impurities commonly present in the substance under examination, nor by the products of the reaction.

In addition to these requirements it is a distinct advantage if the color reaction is equally decided in alcoholic as in aqueous liquids.

**Litmus.**—The coloring principles of litmus are azolitmin, erythrolitmin, and erythrolein. The first, which is the most important, is soluble in water, but insoluble in alcohol. The other two are readily soluble in alcohol, but only sparingly soluble in water.

The U. S. P. process for making litmus test-solution, consists in exhausting coarsely powdered litmus with boiling alcohol.

The residue is then digested with about an equal

weight of cold water so as to dissolve the excess of alkali present.

The blue solution thus obtained, after being acidulated may be used to make *red litmus-paper*. Finally, the residue is extracted with about five times its weight of boiling water, and the solution filtered.

The filtrate is preserved as *test solution*, in wide-mouthed bottles, stoppered with loose plugs of cotton to exclude dust, but to admit air.

When kept in closed vessels litmus solution gradually loses color, but this returns upon exposure to air and consequent absorption of oxygen.

The fermentation to which the loss of color is due may be prevented by saturating the solution with NaCl.

The British Pharmacopœia recommends to boil the litmus in powder with three successive portions of rectified spirit, and then to digest the residue in distilled water, and filter, the object of these steps in the process being to get rid of the greater portion of erythrolitmin and erythrolein, which are soluble in alcohol. Then by treating the residue with water a larger proportion of azolitmin is dissolved, and the solution is contaminated with very little of the other two principles.

Litmus may be used in a very large number of titrations. It is of value in the titration of most mineral acids and of a few organic acids, e. g., benzoic and oxalic. It is also useful in the titration of alkaline hydroxides when the latter are free from carbonates.

But for carbonates, bicarbonates, etc., a reliable end reaction can only be obtained by boiling the solution during the titration, in order to dispel the liberated  $\text{CO}_2$ .

Free  $\text{CO}_2$  has an acid reaction with litmus, and interferes very much with the finding of the end reaction.

Litmus may be used for ammonia and for borax. It is of no use for phosphoric or arsenic acid, nor for phosphates or arsenates, because the change of tint is too gradual.

It is unsatisfactory in titrating many organic acids, e.g., tartaric and citric.

Sometimes it is required to perform a titration with litmus at night. Gas or lamp light is not adapted for showing the reaction satisfactorily, but by using a monochromatic light, such as the sodium flame, a very sharp line of demarcation may be found.

The operation should be conducted in a dark room; using a piece of platinum-foil sprinkled with salt or a piece of pumice-stone saturated with a solution of salt, heated in a Bunsen flame.

The red color then appears perfectly colorless, while the blue appears like a mixture of ink and water.

**Phenolphthalein.**—*Preparation.*—5 parts of phthalic anhydride ( $\text{C}_8\text{H}_4\text{O}_3$ ), 10 parts of phenol ( $\text{C}_6\text{H}_5\text{OH}$ ), and 4 parts of  $\text{H}_2\text{SO}_4$  are heated together at  $120^\circ$  to  $130^\circ$  C. for several hours. The product is then boiled with water, and the residue, which consists of impure phenolphthalein, is dissolved in dilute soda solution and filtered. By neutralizing this solution the phenolphthalein is precipitated, and may be purified by crystallization from alcohol; or the alcoholic solution may be boiled with animal charcoal, filtered, and the phenolphthalein reprecipitated by boiling water.

*Uses.*—Phenolphthalein is a very valuable indicator; it is extremely sensitive, and exhibits a well-marked and prompt change from colorless to pink, and *vice versa*.

A few drops of the solution of the indicator show no color in neutral or acid liquids, but the faintest excess of alkali produces a sudden change to red.

It may be employed in the titration of mineral and organic acids and most alkalies, but it is not suited for the titration of ammonia or its salts. It is very sensitive to  $\text{CO}_2$ , and therefore in estimating carbonates the liquid must be boiled, as with litmus. It is inapplicable for borax, because the color gradually fades away as the acid is added. One great advantage which phenolphthalein possesses is that its indications may be clearly read in many colored liquids; another is that it may be used in alcoholic liquids or in mixtures of alcohol and ether, and therefore many organic acids which are insoluble in water may be accurately titrated by its help.

**Phenolphthalein T. S.** is prepared as follows: Dissolve 1 gm. of phenolphthalein ( $\text{C}_{20}\text{H}_{14}\text{O}_4$ ) in 100 cc. of diluted alcohol U. S. P.

**Methyl-orange.**—Porrier's Orange III, Tropæolin D, Helianthin, Mandarin-orange, para-sulpho-benzene-azo-dimethylaniline.

This is prepared by the action of diazo-sulphanilic acid upon dimethylaniline; the acid so formed is converted into a sodium or ammonium salt, purified by reprecipitation with  $\text{HCl}$ , and again converted into a sodium or ammonium salt. If prepared carefully and from the purest materials, it is a bright orange-red powder, perfectly soluble in water and slightly soluble in alcohol; but it is often found in commerce as a dull orange-brown powder, often not completely soluble in water. Many conflicting statements have been made by operators as to the value of methyl-orange as an



indicator, which have tended to bring this indicator into disrepute.

Sutton has examined many specimens, but has not found any in which the impurities sensibly affected its delicate action. He claims that the common error is the use of too much indicator, and that some eyes are more sensitive to a change of tint than others.

Methyl-orange is no doubt a very good indicator, but practice with it must be had, in order to obtain good results. The author has found one sample which had a beautiful orange color, but which was absolutely useless as an indicator.

A. H. Allen describes as follows the characters and tests of a good article :

1. Aqueous solution, not precipitated by alkalies. (Orange I becomes red-brown; orange II brownish red.)

2. Hot concentrated aqueous solution yields with HCl microscopic acicular crystals of the free sulphonic acid, soon changing to small lustrous plates or prisms having a violet reflection. (Orange I gives yellow-brown color or flocculent precipitate; orange II brown-yellow precipitate.)

3. Dissolves in concentrated  $\text{H}_2\text{SO}_4$  with a reddish or yellowish-brown color, which on dilution becomes fine red.

4.  $\text{BaCl}_2$  yields a precipitate.

5.  $\text{CaCl}_2$  yields no precipitate. Orange I gives a red precipitate.)

6.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  yields an orange-yellow precipitate.

7.  $\text{MgSO}_4$  in dilute solutions precipitates the coloring matter in microscopic crystals.

Methyl-orange T. S. is made by dissolving 1 gm.



of methyl-orange in 1000 cc. of water. Add to it carefully diluted sulphuric acid in drops, until the liquid turns red and just ceases to be transparent. Then filter.

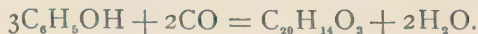
The great value of this indicator consists in the fact that it is not affected by carbonic-acid gas, sulphuretted hydrogen, or boric, silicic, arsenous, oleic, stearic, and many other acids.

It answers well for ammonia, but it is useless for most of the organic acids. Phosphoric and arsenic acids are rendered neutral to methyl-orange when only one third of the acid has combined with the base, the end reaction being well defined. (Phenolphthalein indicates neutrality when two thirds of acid are combined.)

**Rosolic Acid**,  $C_{20}H_{14}O_3$ .—This compound is also called Aurin and Corallin, and is prepared as follows:

A mixture of phenol and sulphuric acid is placed upon a water-bath, and oxalic acid gradually added, waiting each time till the evolution of gas ceases, and using less oxalic acid than is required to attack all the phenol.

In this process the oxalic acid is decomposed into CO,  $CO_2$ , and  $H_2O$ . The CO immediately reacts with the phenol and forms rosolic acid, as the following equation shows:



Rosolic acid is soluble in 50% alcohol. Its color is pale yellow, unaffected by acids, but turning violet-red with alkalis.

It is an excellent indicator for all the mineral acids, but is not reliable for the organic acids, excepting oxalic,

**Rosolic-acid Test Solution, U. S. P.**—Dissolve 1 gm. of commercial rosolic acid (chiefly methylaurin,  $C_{20}H_{16}O_3$ ) in 10 cc. of diluted alcohol, and add enough water to make 100 cc. The solution turns violet-red with alkalis, yellow with acids. In place of rosolic acid, commercial pæonin (also known as aurin R) [chiefly  $C_{19}H_{14}O_3$ ] may be employed.

**Fluorescein** or Resorcin Phthalein  $C_{20}H_{12}O_5$ , is prepared by heating resorcin with phthalic anhydride to  $200^\circ$  C. Dark-brown crystals are formed, which dissolve in ammonia, forming a red solution, with a splendid green fluorescence.

**Fluorescein Test Solution, U. S. P.**—Agitate 1 gm. of fluorescein with 100 cc. of diluted alcohol until the latter is saturated; then filter.

**Eosin**, or Tetra-bromo-resorcin-phthalein.—This is made by adding bromine to a solution of fluorescein in glacial acetic acid. Crystals gradually separate, which may be purified by conversion into a potassium salt and precipitated with an acid.

The composition of this substance is  $K_2C_{20}H_6Br_4O_3$ .

**Eosin Test Solution, U. S. P.**—Dissolve 1 gm. of commercial yellowish eosin in 30 cc. of water.

**Corallin Test Solution, U. S. P.**—Dissolve 1 gm. of corallin (a coloring matter derived from coal-tar, and containing rosolic and para-rosolic acids) in 10 cc. of alcohol and enough water to make 100 cc.

**Gallein.**—Anthracene violet or pyrogallo-phthalein was proposed by M. Dechan for use as an indicator.

It is prepared by heating a mixture of one part of phthalic anhydride and two parts of pyrogallol, and finally recrystallizing in a similar way to phenolphthalein.

It is described as a dark reddish crystalline solid, possessing a greenish lustre. It is nearly insoluble in water, but readily soluble in alcohol. In commerce it is frequently found as a paste, mixed with water.

It forms a violet-pink coloration with alkalies, which is changed to yellowish brown on addition of an acid in excess.

It is said to be more delicate towards alkalies than phenolphthalein, and may be used in its stead for titrating many of the alkaloids. It may be used in the presence of ammonia or its salts. It indicates sharply with the organic acids. A solution in rectified spirit 1-1000 is generally employed.

**Lacmoid** is somewhat allied to litmus, but differs from it in many respects. It is a product of resorcin, and may be prepared by heating gradually to  $110^{\circ}$  C. a mixture of 100 parts of resorcin, 5 parts of sodium nitrite, and 5 parts of water. After the violent reaction moderates it is heated to  $120^{\circ}$  C. until ammonia ceases to be evolved. The residue is then dissolved in warm water and the lacmoid precipitated therefrom by HCl; the free acid is then removed by washing and the residue dried.

Lacmoid is soluble in dilute alcohol. A solution containing 2 gms. in a litre is generally employed.

**Lacmoid Paper.**—This is prepared by dipping slips of calendered unsized paper into the blue or red solution and drying them.

Lacmoid is affected by carbonic-acid gas. It may be used cold for the alkaline and earthy hydroxides, arsenites, and borates, and the mineral acids. The carbonates and bicarbonates of the alkalies and alkaline earths are titrated hot with this indicator.

Many of the metallic salts, such as the sulphates and chlorides of iron, copper, and zinc, which are more or less acid to litmus, are neutral to lacmoid; therefore free acids in such solutions may be estimated by its aid.

Lacmoid paper reacts alkaline with the chromates of potassium or sodium, but neutral with the dichromates, so that a mixture of the two or of chromic acid and dichromate may be titrated by its aid.

**Phenacetolin.**—This may be prepared by boiling together for several hours equal molecular proportions of phenol, acetic anhydride, and sulphuric acid. The product is then well washed with water to remove excess of acid, and dried for use. It is soluble only in alcohol, and a convenient strength of solution is 2 gms. per litre. The solution is dark brown, which gives a scarcely perceptible yellow with caustic soda or potassa, when a few drops are used with the ordinary volumes of liquid. With the normal alkaline carbonates and with ammonia it gives a dark pink, with bicarbonate a much more intense pink, and with the mineral acids a golden yellow.

This indicator may be used for estimating the amount of caustic potash or soda in the presence of their normal carbonates. Practice is, however, required, so as to acquire knowledge of the exact shades of color.

**Cochineal Test Solution, U. S. P.**—Macerate 1 gm. of unbroken cochineal during four days with 20 cc. of alcohol and 60 cc. of water, then filter. The color of this test solution turns violet with alkalis and yellowish red with acids.

**Brazil-wood Test Solution, U. S. P.**—Boil 50 gms.

of finely cut Brazil-wood [the heart-wood of *Pithecellobium dubium* (Sprengel) Britton, nat. ord. *Leguminosæ*] with 100 cc. of water during half an hour, replacing from time to time. Allow the mixture to cool; strain; wash the contents of the strainer with water until 100 cc. of strained liquid are obtained; add 25 cc. of alcohol and filter. This solution turns purplish red with alkalis and yellow with acids.

**Turmeric Tincture, U. S. P.**—Digest any convenient quantity of ground curcuma-root [from *Curcuma longa* Linné, nat. ord. *Scitamineæ*] repeatedly with small quantities of water, and throw this liquid away. Then digest the dried residue for several days with six times its weight of alcohol, and filter.

**Turmeric Paper.**—Impregnate white, unsized paper with the tincture and dry it.

#### REAGENTS AND TEST SOLUTIONS.

**Ammonium-carbonate Test Solution.**—10 gms. of ammonium carbonate  $\text{NH}_4\text{HCO}_3$ ,  $\text{NH}_4\text{NH}_2\text{CO}_2$  are dissolved in a mixture of 10 cc. of ammonia-water and 40 cc. of water.

**Ammonium-chloride Test Solution.**—10 gms. of  $\text{NH}_4\text{Cl}$  are dissolved in sufficient water to make 100 cc.

**Ammonium-molybdate Test Solution.**—1 gm. of finely powdered ammonium molybdate  $(\text{NH}_4)_2\text{MoO}_4$  is dissolved in 6.7 cc. of hot water, using a little ammonia-water, if necessary, to effect solution; the liquid is then poured gradually into a mixture of 3.3 cc. of nitric acid (sp. gr. 1.414) and 3.4 cc. of water.

The solution should be preserved in the dark, and if a sediment should form in it after some days, carefully decant the clear solution from it.

**Ammonium-oxalate Test Solution.**—1 gm. of pure crystallized ammonium oxalate in sufficient water to make 100 cc.

**Barium-chloride T. S.**—12.2 gms. of the pure salt in enough water to make 100 cc.

**Cupric-sulphate T. S.**—10 gms. of  $\text{CuSO}_4 + 5\text{H}_2\text{O}$  in water to make 100 cc.

**Ferric-ammonium Sulphate T. S.**—10 gms. of ferric ammonium sulphate in water to make 100 cc.

**Hydrochloric Acid, Pure, for Tests, HCl.** See U. S. P.

**Indigo T. S.**—Place 6 gms. of fuming sulphuric acid into a beaker well cooled by immersion in water, and stir into it very gradually 1 gm. of finely powdered Bengal indigo. Set the mixture aside for two days, then pour it into 20 cc. of water, and decant. Or, dissolve 1 gm. of commercial indigo-carmin (the sodium or potassium salt of sulphindigotic acid) in 150 cc. of water.

**Iodine T. S.**—Iodine 1 gm., potassium iodide 3 gms., water 50 cc.

**Iron (Metallic) Fe.**—See U. S. P.

**Magnesium Sulphate T. S.**—10 gms. of  $\text{MgSO}_4 + 7\text{H}_2\text{O}$  in water to make 100 cc.

**Nitric Acid, Pure, for Tests,  $\text{HNO}_3$ .**—See U. S. P.

**Potassium Chromate T. S.**—Dissolve 1 gm. of  $\text{K}_2\text{CrO}_4$  in enough water to make 10 cc. On adding silver nitrate T. S. to a little of the solution a red precipitate is produced, which should be completely dissolved by nitric acid (absence of *chloride*). Another portion of the solution mixed with an equal volume of diluted hydrochloric acid should yield no precipitate with barium chloride T. S. (absence of *sulphate*).



**Potassium Ferricyanide T. S.**—1 part of  $K_3Fe(CN)_6$  in about 10 parts of water. Should be freshly prepared when wanted.

**Potassium Hydroxide T. S.**—Use the official liquor potassæ.

**Potassium Iodide T. S.**—16.556 gms. of KI in enough water to make 100 cc. The solution should be kept in dark-amber colored, well-stoppered bottles to prevent the formation of iodate. It is well to renew it frequently or prepare it freshly when wanted.

**Silver Nitrate T. S.**—For ordinary purposes use the decinormal volumetric solution.

**Sodium Hydroxide T. S.**—Use the official liquor sodæ.

**Starch T. S.**—Mix 1 gm. of starch with 10 cc. of cold water, and then add enough boiling water, under constant stirring, to make 200 cc. of a thin, transparent jelly.

**Sulphuric Acid, Pure, for Tests,  $H_2SO_4$ .**—See U. S. P.

For other test solutions see the United States Pharmacopæia.





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